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BIOCATALYSIS

BIOCATALYTIC PRODUCTION OF 5-CYANOVALERAMIDE FROM ADIPONITRILE

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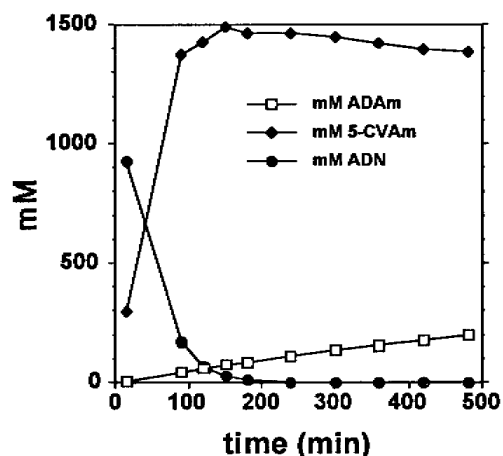
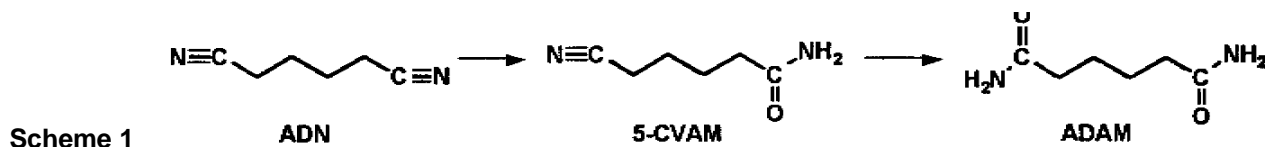
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Abstract

A biocatalytic process for the hydrolysis of adiponitrile to 5-cyanovaleramide has been developed which can be run to higher conversion, produces more product per weight of catalyst, and generates significantly less waste products than the best chemical process. The biocatalyst consists of *Pseudomonas chlororaphis* B23 microbial cells (Nitto Chemical Industry Co.) immobilized in calcium alginate beads. The cells contain a nitrile hydratase enzyme which catalyzes the hydrolysis of adiponitrile to 5-cyano-valeramide with high regioselectivity, and with less than 5 % selectivity to byproduct adipamide. Fifty-eight consecutive batch reactions with biocatalyst recycle were run to convert a total of 12.7 metric tons of adiponitrile to 5-cyanovaleramide. At 97 % adiponitrile conversion, the yield of 5-cyanovaleramide was 13.6 metric tons (93 % yield, 96 % selectivity), and the total weight of 5-cyanovaleramide produced per weight of catalyst was ca. 3,150 kg/kg (dry cell weight).

Introduction

5-Cyanovaleramide (5-CVAM) was required as a starting material for the synthesis of a new agrochemical product. A chemical hydrolysis of adiponitrile (ADN) using manganese dioxide as catalyst was developed (Scheme 1), but this process suffered from several problems: (1) the manganese dioxide was not reusable, (2) it was difficult and expensive to recover and reactivate the catalyst, (3) significant adipamide (ADAM) was produced at > 20 % conversion of ADN, and (4) it was difficult to separate 5-CVAM from unreacted ADN for recycle of ADN to the hydrolysis reaction. As an alternative to the chemical hydrolysis of ADN to 5-CVAM, a process which utilizes a biocatalyst was developed which alleviated all of the problems associated with the chemical process, and which produced significantly less waste.



Summary

Screening of a variety of microorganisms as catalyst for the hydrolysis of ADN led to the identification of several bacteria which contained a nitrile hydratase (EC 4.2.1.84) which could regioselectively produce 5-CVAM in high yield. Further screening of catalyst stability and productivity led to the selection of *Pseudomonas chlororaphis* B23¹ (Nitto Chemical Industry Co.) as catalyst for production of 5-CVAM (Figure 1).

Figure 1. Time course for conversion of 16.2 wt % ADN using 10.1 wt % B23/alginate bead catalyst in 23 mM sodium butyrate (pH 7.0), 5 mM calcium chloride at 5 °C.

The inclusion of sodium butyrate in the reaction mixture significantly improved catalyst stability, and a low concentration of calcium chloride was added to maintain the integrity of alginate-immobilized whole cell catalyst. In the first commercial-scale demonstration of the process, 167 lb (5.8 wt % of reaction mass) of B23/alginate beads were employed to convert 480 lb of ADN (16.8 wt %) in each of 58 consecutive batch reactions. At 97 % adiponitrile conversion, the yield of 5-CVAM was 13.6 metric tons (93 % yield, 96 % selectivity), and the total weight of 5-CVAM produced per weight of catalyst was ca. 3,150 kg/kg (dry cell weight). In comparison with the use of manganese dioxide, which produced 1.26 lb of MnO₂/celite as waste per pound of 5-CVAM produced, only 0.006 lb of B23/alginate bead waste was produced per pound of 5-CVAM produced.

Reference

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CONSTRUCTION AND CHARACTERIZATION OF A RECOMBINANT *PSEUDOMONAS PUTIDA* FOR THE BIOCONVERSION OF TOLUENE TO *p*-HYDROXYBENZOATE

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ABSTRACT

Biocatalytic production of *p*-hydroxybenzoate (HBA) provides improved regiospecificity over Kolbe-Schmitt carboxylation of phenol while minimizing byproduct generation. Toluene bioconversion to HBA by a recombinant *Pseudomonas putida* involved generating a non HBA degrading mutant *P. putida* strain, EM2839, using nitroso-guanidine mutagenesis. Mini-Tn5 transposon systems with regulated *P_{trc}* and *P_{sal}* promoters were used to integrate the genes encoding toluene-4-monooxygenase (T4MO), *p*-cresol methylhydroxylase (PCMH), and *p*-hydroxybenzaldehyde dehydrogenase (PHBZ) onto the chromosome of *P. putida* EM2839 and allow for the independent regulation of T4MO from PCMH and PHBZ. Stability studies in batch cultures without selection pressure revealed that 90 to 100% of the culture retained the transposon system after 86 generations. Two bottlenecks limited carbon flux through the pathway. First, low T4MO activity leads to a maximum HBA production rate of 1.63 ± 0.10 nmol min⁻¹ mg protein⁻¹ by resting cells of *P. putida* EM2878. Second, the higher specificity of PCMH for *p*-cresol than *p*-hydroxybenzyl alcohol causes a transient accumulation of *p*-hydroxybenzyl alcohol in batch bioconversion studies of *p*-cresol to HBA. Furthermore, in the *p*-cresol to HBA transformation studies, HBA production from *p*-cresol was nonlinear with a maximum rate of 17 ± 0.75 nmol min⁻¹ mg protein⁻¹ while *p*-cresol disappearance was measured to be 26 ± 5.1 nmol min⁻¹ mg protein⁻¹. In addition to toluene, this system will also catalyze the conversion of various 2- and 3-substituted toluenes to 2- and 3-substituted *p*-hydroxybenzoates, which may be used as monomers in the production of liquid crystal polymers.

INTRODUCTION

HBA is used as an intermediate in the manufacturing of dyes, pesticides, pharmaceuticals, and preservatives; to which ca. 490 ton/yr are produced as methyl, ethyl, and *n*-propyl parabens³. It is also the chief monomer used in the production liquid crystal polymers (LCP's), a 4550 ton/yr industry, largely owing to its cost advantage relative to other polynuclear aromatic monomers. The demand for HBA is expected to increase as the use of LCP's in the microelectronics industry expands with the rising demand for smaller and faster microelectronics, and the industry switches to surface mount technology.

HBA is synthesized industrially by the Kolbe-Schmitt carboxylation of potassium phenolate under an excess carbon dioxide atmosphere at 220°C and 0.45 MPa for 4 to 8 hours. 48% of the available potassium phenolate is converted to HBA, while 12% is converted to *o*-hydroxy-benzoic acid and 4-hydroxyisophthalic acid byproducts as a result of a lack of absolute regiospecificity. The remaining potassium phenolate is oxidized back to phenol (40%)⁷. Process emissions include phenol discharge from gas and waste water streams which is regulated by the Clean Air and Water Act, and metal salts and heavy residues which are becoming increasingly expensive to landfill and incinerate. Furthermore, the process could be subject to mandated reductions in CO₂ gas emissions, which have been the focus of recent world politics in an effort to slow the cause of global warming⁹. In view of the growing emphasis placed on environmentally benign synthesis strategies, alternatives to current technology yielding higher selectivity and minimal waste generation would be highly desirable.

The goal of this research is to develop a biocatalyst that can be used as a general reagent to augment the traditional synthesis of HBA. In our quest to achieve this goal we seek to exploit 2 intrinsic characteristics of biocatalysis, the regioselectivity of enzyme catalyzed reactions and the ability to carry out sequential reactions in a single organism. As a model biosynthetic process, we chose to study the bioconversion of toluene to HBA using a single recombinant organism. We describe in this paper the initial construction of a recombinant *Pseudomonas putida* that was engineered to overexpress pathway genes obtained from various *Pseudomonas* sp. for the conversion of toluene to HBA. Bottlenecks to carbon flux through the pathway are discussed in addition to HBA production kinetics and overall catalyst performance. The substrate range of the biocatalyst was also investigated with the goal of extending its use to the production of substituted hydroxybenzoates that can be used as monomers in the synthesis of LCP's.

SUMMARY

Central to the conversion of toluene to HBA in *P. putida* EM2878 is the toluene-4-monooxygenase system (T4MO) from *P. mendocina* KR1. T4MO is a 4-component monooxygenase that catalyzes the conversion of toluene to *p*-cresol by regioselective incorporation of 1 atom of O₂ into the aromatic ring^{8,11}. Transformation of *p*-cresol to *p*-hydroxybenzaldehyde is catalyzed by *p*-cresol methylhydroxylase (PCMH), a cytochrome c:flavoprotein from *P. putida* NCIB9869 that incorporates the oxygen from water into the methyl group of *p*-cresol to give *p*-hydroxybenzyl alcohol, followed by dehydrogenation to give *p*-hydroxybenzaldehyde⁵. The final step, dehydrogenation of *p*-hydroxybenzaldehyde to HBA, is catalyzed by PHBZ, an aromatic aldehyde dehydrogenase also from *P. putida* NCIB9869⁴. The reaction sequence is given in Figure 1.

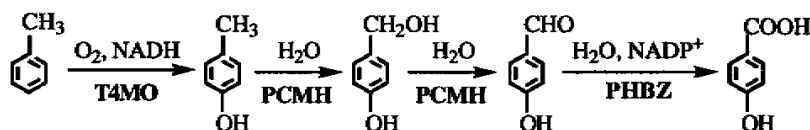
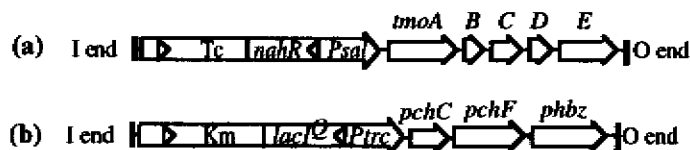


Figure 1. Toluene bioconversion pathway to HBA by *P. putida* EM2878.

Biocatalyst construction required blocking native HBA degradative activity and the stable recruitment of pathway genes into a single organism. N-methyl-N'-nitro-nitrosoguanidine mutagenesis was employed to disrupt *PobA*, the enzyme that catalyzes the *meta* hydroxylation of HBA to protococatechuate in the degradation of HBA². After d-cycloserine/piperacillin enrichment, 3000 colonies were screened for the loss of *PobA* activity by counter selection on HBA supplemented minimal media plates. Of these, 4 colonies were shown to be deficient in *PobA* activity following activity assay of crude enzyme extracts. Both HBA and *p*-hydroxybenzaldehyde were used as inducers to distinguish between loss of *PobA* activity and loss of the HBA transport system. One *pobA*⁻ mutant from the original 4 was selected at random to be the host of the recombinant system and was designated *P. putida* EM2839.

The mini-Tn5 transposon systems described by deLorenzo et al.¹ were modified to allow for the screening of multiple transpositions and the stable recruitment of pathway genes in the absence of selection pressure. The pathway was constructed using two independent promoters, *P_{trc}* and *P_{sal}*. This afforded the independent regulation of the 5 T4MO structural genes, *tmoABCDE*, from the down stream genes, *pchCF*, and *phbz*, encoding active PCMH and PHBZ enzymes, respectively. A schematic of the resulting transposon constructions is shown in Figure 2. Each of the transposon constructions were mated into *P. putida* EM2839 using *E. coli* S17-1λpir as donor strain. After screening for the presence of both transposons using kanamycin and tetracycline resistance markers, and confirming enzyme activity, the resulting strain was designated *P. putida* EM2878.

Figure 2. Construction and organization of regulated transposon systems. (a). Organization of *tmoABCDE* genes encoding active T4MO. (b). Organization of *pchCF* and *phbz* genes encoding active PCMH and PHBZ, respectively. Protocols for DNA isolation and purification were as previously described¹⁰. Restriction digests and ligations were performed as per enzyme supplier's protocols.



Following induction of enzyme activity, the conversion of toluene to HBA by resting cell suspensions of *P. putida* EM2878 was performed in 0.6% glutamate minimal media supplemented with 2 mM IPTG and 3 mM salicylate, 500 µg/ml chloramphenicol to stop further protein synthesis, and 0-1.5 mM toluene using screw top flasks sealed with teflon backed septa. Samples were withdrawn periodically with a syringe, clarified by centrifugation, and analyzed by HPLC using a Waters 990 Diode Array Detector. Conversion of toluene to HBA was stoichiometric, indicating no degradative losses of product. The selectivity of the reaction was 99+% for *para* substituted product. Maximum conversion of toluene to HBA was achieved in about 4 hours with a maximum yield of 0.08 mM to 0.11 mM. HBA production followed Monod kinetic dependence on toluene, yielding $V_{\max} = 1.63 \pm 0.10$ nmol min⁻¹ mg protom⁻¹ and $K_m = 58 \pm 5$ µM.

Two bottlenecks to carbon flux were found to limit toluene bioconversion to HBA in *P. putida* EM2878. The first is caused by a low level of T4MO activity that results in a slow turnover of toluene to *p*-cresol and is independent of the promoter configuration used to express the *tmoABCDE* genes. This was shown by spiking resting cells of *P. putida* EM2878 with varying levels of *p*-cresol during toluene bioconversion. The HBA profiles generated during this experiment are shown in Figure 3(a). Upon *p*-cresol addition an increase in the rate of HBA production

results, apparently due to the excess capacity that exists downstream of the T4MO step even in the absence of further enzyme synthesis. The second bottleneck is due to the specificity of PCMH for *p*-cresol ($K_m = 16\mu\text{M}$) than *p*-hydroxybenzyl alcohol ($K_m = 27\mu\text{M}$)⁶. The increased specificity gives rise to a transient accumulation of *p*-hydroxybenzyl alcohol during *p*-cresol bioconversion to HBA. This can be seen in the concentration profiles in Figure 3(b). In these experiments HBA production from *p*-cresol was nonlinear with a maximum rate of $17 \pm 0.75 \text{ nmol min}^{-1} \text{ mg protein}^{-1}$ while *p*-cresol disappearance was measured to be $26 \pm 5.1 \text{ nmol min}^{-1} \text{ mg protein}^{-1}$.

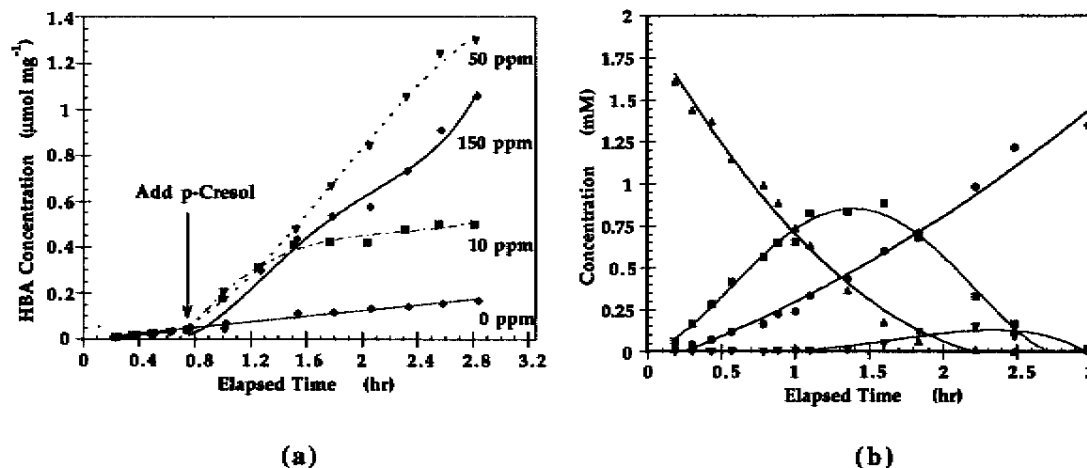


Figure 3. Carbon flux bottlenecks in toluene bioconversion by resting cells of *P. putida* EM-2878. (a) Identification of T4MO rate limiting step. Concentrations at right denote amount of *p*-cresol added. (b) Transient accumulation of *p*-hydroxybenzyl alcohol in conversion of *p*-cresol to HBA. (○) *p*-cresol; (□) HBA; (△) *p*-hydroxybenzaldehyde; (◇) *p*-hydroxybenzyl alcohol. Lines drawn to indicate trends.

In addition to determining the HBA production kinetics, studies were undertaken to determine the substrate range of *P. putida* EM2878 in overnight incubations. Substrate modifications included methyl group replacement with ethyl and *n*-propyl functional groups, in addition to adding chloro, methyl, amino, and nitro functional groups to the 2 and 3 positions on the aromatic ring. Preliminary analysis of HPLC data suggests that ethylbenzene may also be a substrate for bioconversion by *P. putida* EM2878 producing 4-ethylphenol and 4-hydroxyacetophenone products. Both *n*-propylbenzene and 4-propylphenol were not substrates for bioconversion, suggesting that both T4MO and PCMH enzymes do not recognize substrates with side chains of greater than 2 carbon atoms in length.

Of the 2-substituted toluenes tested, only *o*-xylene was found to undergo bioconversion giving 4-hydroxy-2-methylbenzoate as a product. 2-Chlorotoluene, 2-aminotoluene, and 2-nitrotoluene did not serve as substrates for conversion to 2-substituted-*p*-hydroxybenzoates. Steric hindrance caused by the larger Cl and NO₂ side groups may inhibit substrate binding in the active site of the T4MO enzyme. 3-Substituted toluenes serving as substrates for bioconversion included both *m*-xylene and 3-chlorotoluene, giving 4-hydroxy-3-methylbenzoate and 3-chloro-4-hydroxybenzoate products, respectively. 3-Nitrotoluene was not a substrate for bioconversion, and products from 3-aminotoluene conversion could not be definitively identified. In contrast, 2-amino-4-methylphenol, and to a lesser extent 4-methyl-2-nitrophenol, were found to be substrates for bioconversion, suggesting that PCMH and PHBZ enzymes may have a slightly broader substrate range than T4MO.

ACKNOWLEDGMENTS

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METABOLIC ENGINEERING FOR THE PRODUCTION OF COMMODITY CHEMICALS

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Microbial fermentation is an important "green" technology for the production of chemicals, especially since it typically involves renewable feedstocks and does not generate toxic byproducts. Fermentation, however, has several well-known limitations compared to chemical synthesis: 1) the range of products is relatively small, 2) the yields, titers and productivities are often low, and 3) recovery and purification of products from aqueous fermentation broths are often difficult. Although there are no simple ways to overcome all of these limitations, they can be significantly reduced through the application of metabolic engineering. For example, new metabolic pathways can be generated by adding or deleting genes. Product yields can be improved by eliminating pathways leading to by-products. The elimination of toxic by-products may lead to increased product titers. Finally, reduced by-product levels and increase product titers may simplify product recovery and purification.

The importance of metabolic engineering for the production of chemicals is illustrated with two examples: the microbial production of 1,3-propanediol (1,3-PD) and the microbial production of 1,2-propanediol (1,2-PD; propylene glycol). The first part of this talk will focus on the specific pathways to 1,3-PD and 1,2-PD. Although the pathways are significantly different; 1,3-PD and 1,2-PD are isomers with similar physical properties. The second part of this talk will focus on features that are common to both fermentations—in particular, strategies for obtaining maximum product yields and the influence of yield and selectivity on product titer and recovery. Lastly, points from the propanediol examples will be used to illustrate the use of metabolic engineering for fermentation process development in general.

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SUPERCRITICAL FLUIDS

COMBINED REACTION/SEPARATION PROCESSES USING CO₂Eric J. Beckman and Dan Hancu

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Carbon dioxide is a relatively environmentally-benign solvent that is also inexpensive and non-flammable. Further, above its readily accessible critical temperature (31°C), CO₂ exhibits complete miscibility with a variety of gases. On the other hand, use of CO₂ requires high absolute operating pressures, and thus higher-than-normal capital costs. Although recovery of dissolved products via flash depressurization is relatively straightforward, this leads to high operating costs due to the need for CO₂ recompression. Nevertheless, there are a number of applications where replacement of typical organic solvents with CO₂ could prove beneficial from both an environmental and cost perspective, provided some constraints are applied. For example, those processes which might benefit from adaptation to CO₂ processing incorporate (a) liquid-liquid extraction vs. water, where use of CO₂ eliminates contamination of the aqueous phase and (b) where gaseous reactants are presently used in liquid systems, where use of CO₂ allows for kinetic control. Some practical constraints include (c) finding means by which products or byproducts can be recovered from CO₂ without depressurization, to minimize recompression costs, and (d) employing CO₂-philic reagents to allow lower operating pressures, while making sure to recycle such materials to minimize their impact on cost.

In this paper we present examples where all of these characteristics can be attained. For example, hydrogen peroxide is typically produced via sequential hydrogenation and oxidation of a 2-ethyl anthraquinone (2EAQ). In the first reactor, the 2EAQ is hydrogenated to a hydroquinone over a palladium/alumina catalyst in an organic solvent mixture, a reaction which is limited by transport of hydrogen from gas to liquid. In the second step, the hydroquinone is oxidized to liberate hydrogen peroxide, which is then stripped into water, and the original 2EAQ, which is then recycled. Replacement of the organic solvent mixture with carbon dioxide (a) allows kinetic control of the reaction by eliminating the gas-liquid interface in the hydrogenation and oxidation reactors, and (b) eliminates the organic contamination of the aqueous phase during the liquid-liquid extraction to recover the product. The product can be recovered without depressurization of the CO₂, eliminating recompression as a factor in process cost. However, typical alkyl anthraquinones are poorly soluble in carbon dioxide, prompting us to synthesize highly CO₂-soluble analogs, which can be recycled through the process. Our results show that the structure of the modified anthraquinone strongly affects the diffusion coefficient of the material within the catalyst pores (and thus the regime over which kinetic control is achieved), as well as the kinetic rate constant and the phase behavior in CO₂.

ONE-STAGE DRAWING OF HIGH MOLECULAR WEIGHT POLY(ETHYLENE TEREPHTHALATE) FIBERS IN SUBCRITICAL AND SUPERCRITICAL CO₂Terry Hobbs and Alan J. Lesser

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Abstract

The effects of draw conditions were studied for melt spun high molecular weight poly(ethylene terephthalate) fibers (PET) fibers in the presence of subcritical and supercritical CO₂. Both in-situ and post treatment mechanical behavior along with morphological characteristics were investigated. Results indicate that fibers soaked in subcritical CO₂ could be drawn to 30% higher draw ratios than that produced by cold drawing. During in-situ drawing, the fibers showed no measurable resistance to deformation until strain hardening occurred. Further, the onset of strain hardening occurred at a lower percent strain when compared to cold drawn fibers. In supercritical CO₂, the fibers showed a decrease in ductility and a significant difference in post-yield deformation. In SC CO₂, lower draw ratios were observed along with diminished mechanical properties. The cold drawn fibers had slightly higher tensile modulus and strength values compared to fibers drawn in subcritical CO₂. However, after one stage drawing, both the cold drawn and subcritical fibers showed superior mechanical properties to one stage drawn solution spun fibers of similar molecular weight.

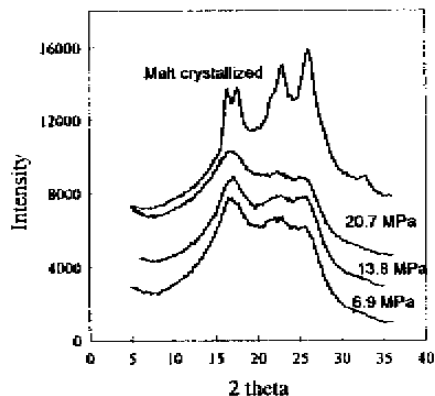
Introduction

The drawing behavior of PET for the production of high modulus and high strength fibers has been studied intensely for the past several years. Although fairly high modulus values of 35 GPa have been reported, it is still difficult to produce high strength fibers. The final strength of a given PET sample is dependent on several factors including sample geometry, entanglement density, load applied during drawing, and molecular weight.¹ Commercial fibers produced by melt spinning have low molecular weight and it is difficult to achieve tenacity and modulus values above a well-established level. Melt spinning of high molecular weight PET is difficult but it is feasible. The melt viscosity is quite high resulting in low fluidity. For this reason, most of the literature has focussed on solution spinning utilizing various organic solvents.² From a processing point of view, these solvents are undesirable since they must be removed which can also create defects in the fiber. In this paper, we investigate the use of subcritical and supercritical CO₂ (SC CO₂) as a drawing media for high molecular weight PET fibers melt spun at a low takeup speed. The emphasis of this paper is to study the first drawing stage along with the initial fiber morphology. The use of subcritical and SC CO₂ have many potential advantages including solvent tunability, suppression of brittle failure due to imposed hydrostatic pressure, environmental friendliness as a benign solvent, and effective plasticization of PET. We will discuss the differences in drawing behavior and structure development of the PET fibers between cold drawn fibers, fibers drawn in subcritical and supercritical CO₂ along with the mechanical properties of drawn fibers.

Experimental

Materials. High molecular weight PET with a reported intrinsic viscosity of 2.01 dL/g was used for all fiber preparations. The polymer powder was dried for 20 hours at 140° C in a vacuum oven. Fibers were melt spun under a nitrogen blanket in a Randcastle microextruder with a die temperature of 295° C. Fiber mechanical properties were very sensitive to melting and die zone temperatures. As-spun fibers were taken up on a spool at a rate of approximately 250 m/min resulting in a final diameter of 67 µm. The fibers had a birefringence of 1.5×10^{-3} while DSC and flat plate WAXD patterns confirmed that the fibers were amorphous.

Measurements. The first stage drawing of the fibers was performed in a custom high pressure drawing apparatus. The apparatus is mounted on an Instron model 1333 tensile testing machine. Coleman grade CO₂ is supplied through a Hydro-pac, Inc. high-pressure carbon dioxide pump. The apparatus is capable of making in-situ force measurements using a calibrated stainless steel cantilever beam and a LVDT with electronics outside of the CO₂ media. Stress measurements were calculated based on fiber linear density of the fiber and nominal strain was calculated based on crosshead and beam displacements. All fiber bundles were drawn at a strain rate of 1 min⁻¹. Single filament tests were performed on an Instron 5564 using a 10 N load cell at a strain rate of 0.1 min⁻¹ and a gauge length of 25 mm. Birefringence and fiber diameter measurements were made using a Olympus polarizing microscope equipped with a 1-20λ Berek compensator. Crystallinity measurements were made with a DSC and by using a density column prepared from n-heptane and CCl₄. Differential Scanning Calorimetry (DSC) was performed using a TA Instruments thermal analyst 2100 with a heating rate of 10° C/min. Wide angle X-ray measurements (WAXD) were made on a Siemens D500 diffractometer with a Ni filtered Cu-Kα source at 40 kV and 30 mA. Scanning electron microscope (SEM) images of gold sputtered samples were obtained using a JEOL 35CF.



Results and Discussion

Initial Morphology. As with traditional organic solvents, treatment with CO₂ under subcritical and supercritical conditions results in small/imperfect crystallites.^{3,4} Figure 1 shows the WAXD scans for various pressures at a soak time of 15 min and 35° C. It is difficult to ascertain if crystallization takes place in the environment or by removal of the CO₂ upon depressurization. In addition, a lower melting endotherm that appears in the DSC scan (Figure 2) as seen for samples treated at lower pressures in CO₂ for extended time periods.⁵

Figure 1. WAXD of CO₂ treated fibers

Surface and Internal Morphology. Fibers drawn in supercritical CO₂ have a smooth surface similar to the as-spun fibers. Solution spun fibers typically have a rough surface which can lower mechanical properties.⁶ While CO₂ can be used as a foaming agent, the treated fibers at 20.7 MPa have a higher density compared to cold drawn fibers at the same drawn ratio of 4 indicating that foaming does not occur and the supercritical fibers have a higher crystallinity, 26.6 % compared to 23.3 %. Crystallinity values measured by DSC were higher but also

showed slightly higher values for the supercritical fibers. Figure 3 shows the surface morphology. Birefringence measurements in figure 4 show that cold drawn fibers have a higher overall orientation as expected because fibers drawn in CO₂ are drawn above T_g. Subcritical drawn fibers show the same behavior as cold drawn fibers with overall lower values. In the polarizing microscope, supercritical drawn fibers have a unique morphology with a very fine brightly colored texture where the other two show very little color.



Figure 2. Comparison of thermograms

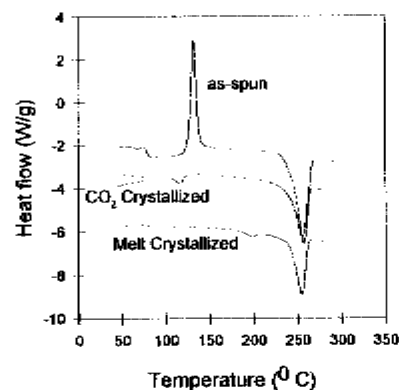


Figure 3. SEM micrograph of CO₂ drawn fibers

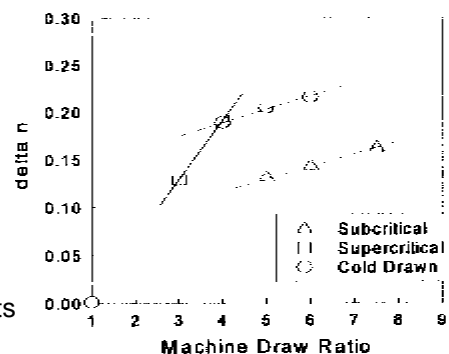


Figure 4. Birefringence measurements

Drawing Behavior. It has been shown that fibers treated with acetone and DMF/water can be drawn to higher draw ratios resulting in higher crystallinities and 20% higher strength values despite a lower amorphous orientation f_a , 0.58 compared to 0.98 for traditional two-stage drawn fibers.⁷ The increased drawability occurred in the first stage and was attributed to plasticization and the imperfect/small crystallites formed.⁸ We see a similar increase in drawability for fibers drawn in subcritical CO₂, however virtually no crystallization is present as shown by the stress/strain behavior in Figure 5. As the soak time reaches 15 minutes, the fibers are completely plasticized and show no mechanical response until 200% strain where the onset of strain induced crystallization occurs early compared to cold drawn samples. In addition, the slope of the stress/strain curve is similar to the cold drawn sample. The increased drawability was confirmed by direct measurements of draw ratio using ink marks placed on the fibers prior to drawing. Figure 6 shows the effect of increasing pressure on the stress/strain behavior after a soak time of 15 minutes. The 6.9 MPa curve is very smooth showing the sensitivity of the apparatus. Again, the fiber bundle shows very little resistance to deformation and the strain induced crystallization slope is lower than that observed in the cold drawn samples. We believe that the main mechanism for increased drawability may be attributed to the hindrance of strain induced crystallization by the presence of CO₂. As the pressure is increased to 13.8 MPa, the density of the CO₂ increases dramatically and crystallization occurs resulting a lower yield response. The polymer network is essentially crosslinked by the crystallites which increases with extension until the fibers begin failing individually in a brittle manner. The stress/strain behavior suggests that a large amount of the crystallization (Figure 1) occurs by CO₂ removal as also noted for fibers crystallized by acetone.⁹

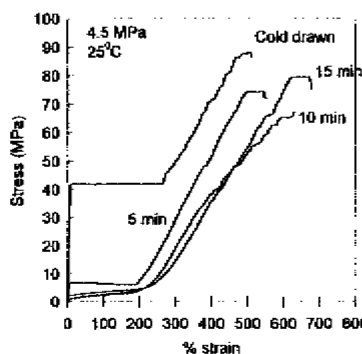


Figure 5. Mechanical behavior as a function of soak time.

Mechanical Properties. The cold-drawn fibers showed better tensile properties when compared to fibers drawn under subcritical (4.5 MPa) and supercritical conditions (20.7 MPa). This is to be expected since all the fibers show low levels of crystallinity (<30%) and the latter two are most likely drawn above their glass transition temperature. The cold drawn fibers should therefore have higher amorphous orientation, which was confirmed by birefringence. Figures 7 and 8 show the tensile modulus and strength values compared to values published in the

literature. The cold drawn and subcritical treated fibers have tensile strengths that are higher than solution spun fibers of similar molecular weight.¹⁰ The fibers are lower compared to solution spun fibers with a much higher molecular weight.¹¹ The supercritical fibers have low tensile values primarily due to the limited draw ratio that was achieved. The modulus of the cold drawn fibers seems to plateau perhaps due to very high amorphous orientation. Finally, the modulus of the subcritical fibers tends to follow moduli of solution cast films of very similar intrinsic viscosity.¹²

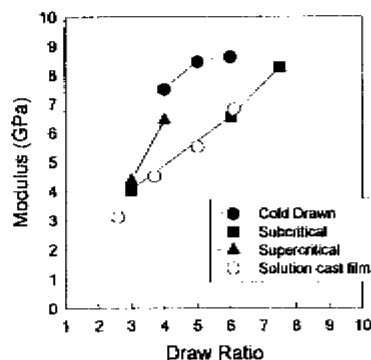


Figure 7. Single Filament Moduli

Figure 8. Tensile strength vs. draw ratio

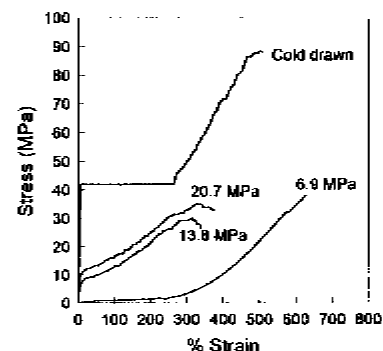
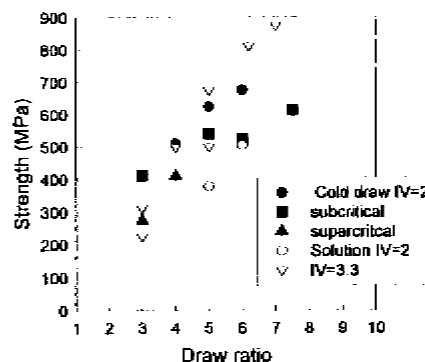


Figure 6. Effect of pressure on drawability.



Summary

PET fibers show improved drawability in a subcritical CO₂ media compared to SC CO₂ and cold draw conditions. The drawability increase is important for second stage drawing. Drawing fibers in SC CO₂ above 13.8 MPa results in higher crystallinity thus limiting the maximum achievable draw ratio. Tensile properties of subcritical and cold drawn fibers were slightly better compared to solution spun fibers of similar intrinsic viscosity.

Acknowledgements

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BUILDING PRODUCTS MADE FROM SUPERCRITICAL CARBON DIOXIDE AND FLY ASH

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Introduction

Coal-fired electric power plant wastes, portland cement, calcium oxide and supercritical carbon dioxide (CO₂) are feedstocks to make low-cost, superior roofing shingles, wallboard and other fiber-reinforced products. Flue-gas CO₂, recovered using thermally-driven, gas-stripping techniques¹, is permanently bound into the products as carbonates, reducing atmospheric pollution and its contribution to global warming.

Abstract

The purpose of this patented technology is to produce profitable building products and many other useful things using cemented "dusty" wastes treated with supercritical CO₂^{2,3}. Products are shaped from a paste made of quick lime, a small amount of portland cement, foamed fly ash and fiberglass reinforcement. Once hydrated, they are treated with supercritical CO₂ (preferably recovered from flue gas) to react the hydroxide components, forming carbonates and water and reducing alkalinity to about neutral.

The process has four important advantages:

1. It is conventional (relies upon proven technology).
2. Capital required is low (three-year plant and equipment payback).
3. Parasitic energy loss to the power plant is low or non-existent.
4. There is a sufficiently high value-added component in final products to offset the logistics costs of raw materials and finished goods.

Production of cementitious goods and gas separation technologies are well-settled. Practical gas-separation technologies can be subdivided into four broad categories⁴:

1. Absorption
2. Membrane separation followed by distillation
3. Membrane absorption
4. Pressure-swing adsorption (PSA)

The appropriate technology depends upon feed stream composition and thermodynamics and upon required quantities of carbon dioxide. In our planned implementation, we will use propylene carbonate absorption. CO₂ stripping will occur after sulfur and nitrogen scrubbing.

Forming fiber-reinforced cementitious products like wallboard and roof shingles is also settled technology. Presently, fiberglass reinforced cementitious products demand costly alkali-resistant or plastic-coated glass to prevent alkali-silica reaction. Supercritical carbonation technology allows use of low-cost e-glass instead.

With the exception of foaming agents, fiber reinforcement and Portland cement, all raw materials are available on site. The lightweight building products (in this case, fiberglass reinforced roofing shingles and fiberglass reinforced wallboard) are made by cementing foamed fly ash (about 53,000 tons annually for this plant) with calcium oxide (quick lime) and a small amount of portland cement. Both products will be made on continuous lines. After cementing, the products are subjected to treatment with supercritical CO₂, again, in a continuous process. The CO₂ forms carbonates and carbonated zeolites and reduces the alkalinity of the product to about neutral (pH 7). This permits incorporation of low-cost e-glass fibers without fear of subsequent, harmful alkali-silica reaction. The reinforcement is in the form of both continuous and chopped fiber.

Samples of the prototype products and those with which they compete will be displayed during the oral presentation.

An analysis of the relative inputs to the prototype shingle compared with competing roofing products indicates that the supercritically treated chemically bonded ceramic shingle will be the least energy intensive⁵.

Based on costs of raw materials and energy, our studies also indicate that we will be able to profitably sell these waste-based products at pricing points significantly below those of the lowest-priced competing products.

A plant to produce both products is expected to cost approximately \$11 million. Based on expected volumes and margins it will be fully amortizable in three years.

These products are examples of practical, solid-waste-feedstock, chemically bonded ceramics. Many other products can be produced in a similar manner, sequestering large quantities of solid waste and CO₂ while offsetting manufacture of products using more energy-intensive systems that increase atmospheric CO₂. Examples of such systems include thermoplastics, metals, composites, ceramics and forest products.

As industrial infrastructure in the developed countries ages and requires replacement or renovation, it will be wise to consider supercritical CO₂ treated chemically bonded ceramics to reduce energy, raw materials and atmospheric pollution. For developing countries, the benefits are even greater.

In a developing economy, the creation of new industrial infrastructure requires huge investments in transportation systems for feedstocks, raw materials and components. Investment is also required to develop primary, secondary and tertiary manufacturing capacity as well as power plants and facilities to dispose of all types of plant wastes at all levels. Supercritical CO₂ chemically bonded ceramic technology reduces much of this investment. Wastes and CO₂ simply replace most feedstocks. Ancillary benefits arise from reduction of capital and energy needed to harvest, mine, or otherwise produce raw materials and transport them and intermediate raw materials for secondary or tertiary manufacturing,

Conclusion

Supercritical CO₂-treated chemically bonded ceramics rely upon proven, practical technology to produce valuable products from solid waste feedstocks. Capital requirements are lower than conventional production systems, particularly when considering cradle-to-grave economics. Parasitic energy loss to producers is essentially none. Profit margins are high, because most products can be produced with low-cost or no-cost feedstocks.

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2nd Annual Green Chemistry &
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BIOSYNTHESIS/ BIOPROCESSING

**Extended abstract not received in time for printing.
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**BIOCOMMODITY ENGINEERING - OPPORTUNITIES,
CHALLENGES, AND GREEN CHEMISTRY**

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The potential of biological processing for environmentally-benign manufacturing is widely and deservedly recognized. Of greatest interest from an environmental point of view are commodity products. Biological production of commodity products differs radically from production of high value products of biotechnology with respect to both economics and technology. In addition, production of high volume, low unit value "biocommodity" products requires high volume, low unit value raw materials - which means plant biomass. Potential biocommodity products will be surveyed with respect to the mix of products that could support a biomass-based chemicals and fuel industry, current and potential production volume, and minimum required feedstock cost. These considerations suggest that most biocommodity products will at least initially be coproduced in a biorefinery rather than in a facility dedicated to a single product. In addition, the range of economically-accessible products can be expected to expand significantly as technology for processing cellulosic materials matures. Two key technical challenges for the emergent biocommodity engineering field are: 1) product diversification, and 2) economically overcoming the recalcitrance of cellulosic materials. Research-driven approaches to meeting these challenges will be discussed. Examples of biocommodity products will be chosen to illustrate potential environmental benefits.

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**DESIGN AND DEVELOPMENT OF SUPER EFFECTIVE *SACCHAROMYCES* YEAST FOR CONVERSION OF
CELLULOSIC BIOMASS TO ENVIRONMENTALLY FRIENDLY TRANSPORTATION FUEL ETHANOL**

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Ethanol is an effective, environmentally friendly, nonfossil transportation biofuel that produces far less pollutants than gasoline and contributes essentially no net carbon dioxide to the atmosphere. Furthermore, unlike crude oil for the production of gasoline, ethanol can be produced from domestically grown, plentifully available, renewable cellulosic biomass which contains two major sugars, glucose and xylose. However, a major obstacle in using this type of feedstocks for ethanol production is that *Saccharomyces* yeast, traditionally used for large scale industrial production of ethanol from glucose, is unable to ferment xylose to ethanol. This makes the use of the safest, most effective microorganism for the conversion of cellulosic biomass to ethanol economically unfeasible. In the Fall of 1993, we achieved a historic breakthrough in the successful development of the first genetically engineered recombinant *Saccharomyces* yeast that can effectively ferment both glucose and xylose to ethanol. This paper will present an up-to-date overview of the design, development, and continuous innovative perfection of our recombinant *Saccharomyces* yeast that is widely regarded as the microorganism making cellulosic biomass to ethanol closer to commercialization.

BIOCONVERSION OF SUGAR CANE VINASSE INTO SCP BY RECOMBINANT STRAINS OF *ASPERGILLUS NIDULANS*

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ABSTRACT

Sugar cane broth is widely used in Brazil in fermentation to produce alcohol. This process yields a large amount of a toxic byproduct, vinasse. Due to its high organic matter, law prohibits its disposal onto rivers. The microbial conversion of the vinasse into Single Cell Protein (SCP) a protein resource and/or methane (fuel) is being evaluated world wide. The present study illustrates approach to single cell protein production based on strains of *A. nidulans* produced through parasexual crossing. Six diploid strains and 23 recombinants were evaluated and compared for their ability in degrading vinasse based on measurement of COD reduction and biomass synthesis. SCP production was based on mycelial dry weight, and indirectly on radial colony growth on Petri dishes. Most of the diploids and certain recombinant strains gave enhanced performance compared to the parental strains.

INTRODUCTION & OBJECTIVE

The Brazilian alcohol project began in 1975 as a result of the world oil crisis. The project peaked in 1986 with a production increase of 37 fold (nearly 12 billion liters/year). In 1996/1997 the production rose and reached 14 billion liters, with one third being anhydrous. During the alcohol distillation process, a byproduct vinasse, is formed. This waste yields an average of 13 parts for each part of alcohol produced. Due to its high organic content, vinasse is prohibited from disposal in rivers. Its composition is variable, being influenced by many factors such as the type of sugar, the composition of the broth, and the distillation process *per se*. However, some features of this byproduct are standard. It is an acidic liquid which is rich in nitrogen, potassium, and organic acids such as succinic and lactic¹, and it contains amino acids, such as leucine, isoleucine and valine². It is poor in sugars and only 10 percent of the total amount of the organic matter is composed of saccharose and fructose³. The pollution index of Chemical Oxygen Demand (COD) is 35 to 60 grams of oxygen per liter, and there is also a large Biochemical Oxygen Demand (BOD₅) which varies from 7 to 20 grams of oxygen per liter.

There are few practical ways to dispose of vinasse, the most usual being its application as a crop fertilizer⁴. This eliminates the waste and also provides nitrogen and potassium as a soil nutrient. Processes aimed at using not just the salts but also the organic content of vinasse were investigated. The aerobic degradation of vinasse to yield microbial Single Cell Protein (SCP) has attracted attention. In this case, the biomass produced is used as a protein source for animal feeding. Bacteria^{2,5}, yeast^{6,7} and filamentous fungi⁸⁻¹² have been evaluated for this purpose.

The aerobic conversion of vinasse into microbial biomass is desirable because it is possible to solve two problems using just one process. When the microorganisms consume vinasse, its toxicity is decreased. The filamentous fungi gave good yield due in part to the secretion of a wide range of enzymes and easy recovery of SCP by filtration. Certain *Aspergillus* species were identified as especially efficient⁸⁻¹².

The main objective of this research was the evaluation of parasexual recombination as a tool for the genetic improvement of *Aspergillus* regarding its ability to use vinasse, using *A. nidulans* as the model system. In doing so, the development work followed three steps. First, establishment of the optimal growth medium. Second, a comparison of *Aspergillus* species, and third, the construction and evaluation of diploids and recombinant strains of *A. nidulans* for vinasse conversion.

MATERIALS & METHODS

Species: *Aspergillus niger* NRRL 337; *A. oryzae* ATCC 7252; *A. sulphureus* IZ (USP) A186; *A. nidulans* strains: Master Strain E (MSE) [*suA1 adeE20 yA2 adeE20; wa3; galA1; pyroA4; facA303; sB3; nicB8; riboB2*]¹³; *Abnc* [*proA1 pabaA6 T (I-II); bncA*]; PPY [*proA1 pabaA6 yA*]; BM [*biA1; methG1*]; INO [*inoB*]; VE [*veA1*]¹⁴. All strains were stocks from ESALQ, -USP from mineral oil or SiO₂.

Medium: the strains were maintained on Complete Medium (CM) for *A. nidulans*¹⁵. The vinasse medium was established in this work; its pH was adjusted to 6.8 with 4N NaOH. For plate assays, 1.5% agar was added.

Sugar Cane Molasses and Vinasse: the sugar cane molasses was donated by a distillery from the Companhia Industrial e Agrícola Ometto, and the vinasse was obtained at the pilot distillery of the Dept. Ciência e Tecnologia Agroindustrial (ESALQ/USP). Both were stored at 1°C.

NPK solution: the commercial fertilizer NPK (10:10:10) was crushed, solubilized (1%) in distilled water, filtered (Whatman #1), autoclaved (1 atm, 20min.) and stored at 4°C.

Radial Growth: the strains were point inoculated on Petri plates containing the appropriate medium for each assay and the colony diameter was measured with the help of a light box.

Dry Biomass Production: the dry biomass production was measured after growing the strain in liquid medium under defined growth conditions. After cultivation, the mycelium was filtered through nylon screen (95 mesh), washed, dried at 70°C until constant weight.

Pollution Indexes: the COD as well the BOD₅ were performed as described in 16. The percent decrease was calculated as a function of the control, uninoculated sample.

Parasexual Crosses, Diploid and Recombinant strains: the parasexual crosses were conducted as described in 15, in which spores from two genetically contrasting strains were cultivated in minimal medium. By this method, diploid cells containing genetic material of both parents were isolated. The derived haploid recombinant strains were obtained by the exposure of the diploid to benomyl, with post recovery of segregated cells from the sectors formed. The diploid condition was confirmed by the ability to grow in minimal medium, by the spore size, and by the capacity to segregate.

RESULTS & DISCUSSION

Medium Establishment: nutrient supplementation of vinasse has been evaluated by other researchers to assess enhancement of biomass productivity^{6,9,11,17}. In our initial trials we attempted to optimize the culture media by using a strain of *A. nidulans* (BM) and evaluating its radial growth using vinasse plus different added compounds. The effects of the addition of sugar cane molasses in increasing concentrations were evaluated. According to the results, optimal radial growth was obtained with the addition of 2% molasses per liter of vinasse (w:v). The addition of a commercial fertilizer with salts of N, P and K (10:10:10) was evaluated. The vinasse appears to have adequate amounts of these components for microbial development, since a decline in their radial growth was observed when these salts were added to the media. Thus in further assays, vinasse medium was standardized as vinasse supplemented with 2% molasses (w:v).

Vinasse Biodegradation by *Aspergillus* species: the next stage was to compare the model *A. nidulans* (Abnc) with other *Aspergillus* species that had been assessed to be efficient in vinasse degradation. These species were *A. niger*, *A. oryzae* and *A. sulphureus*. The first trial was to determine a common temperature for growth of all 4 species. For that purpose we measured the radial growth of the species on solid vinasse medium at three different temperatures (27, 32 and 37°C) twice (after 35 and 70 hours of cultivation). All the species grew well at 32°C and this temperature was subsequently used. After, the 4 species were evaluated for biomass production and COD and BOD₅ reduction. The species were cultured in liquid vinasse medium at 32°C with agitation. The results varied significantly with species (Table 1). Two groups were separated by the Tukey test for biomass production and BOD₅ reduction. There was a low correlation between the dry biomass produced and the radial growth measurements, but a correlation of 0.7 was found between the COD and BOD₅ reduction and *A. nidulans* was identified as the best converter.

Vinasse Conversion by Recombinant Strains of *A. nidulans*: the diploid strains were constructed by parasexual crosses using four genetically contrasting strains as parents, namely M (MSE), P (PPY), B (BM) and I (INO). The combination of these strains resulted in 6 diploid strains: M//P, M//B, M//I, P//B, P//I and B//I. Four recombinants were isolated by haploidization from each diploid. The prototrophic haploid strain VE was used as a control. Next, a determination was made of the growth kinetics and the time required for the culture to attain the stationary phase of development. We evaluated biomass production and radial growth of five strains (M, P, B, M//P, M//B). In both cases, the results suggest that the prototrophic diploid strains started their log phase of growth earlier than the auxotrophic haploids. The control VE was not assayed. No correlation was observed between the strain performance and spore viability. The time yielding an average of 90% of the maximum biomass production for all strains was 43 hours. This culture period was used for further cultivation.

Table 1. Biomass Production and Pollution Reduction of Vinasse by *Aspergillus* species¹

Species	Dry Biomass (mg)	Productivity (g/L/hour)	COD		BOD ₅	
			Reduction (%) ²	Conversion (%) ³	Reduction (%) ⁴	Conversion (%)
<i>A. nidulans</i>	507 a ⁵	0.267	31.12 c	3.06	55.85 ab	6.58
<i>A. niger</i>	493 a	0.260	48.27 a	1.92	61.88 a	5.78
<i>A. oryzae</i>	369 b	0.194	43.42 b	1.60	57.96 A	4.61
<i>A. sulphureus</i>	407 b	0.215	34.73 c	2.21	50.51 b	5.85

¹Incubation Conditions: 7×10^6 spores, 50 mL vinasse medium (Erlenmeyer 250mL), 32°C, 40 hours, agitation of 120 rpm, 3 replicates.

²Average from 2 digestions from a compost sample constituted by the 3 replicates.

³Biomass produced (g) / COD or BOD₅ consumed (g)

⁴Average from 4 digestions (2 by each dilution) from a compost sample constituted by the 3 replicates.

⁵Letters represent the groups formed by the Tukey test (5% confidence), same letters represent no significant variation.

The growth of parental, diploid and recombinant strains of *A. nidulans* in liquid vinasse medium was compared to evaluate their SCP production and COD reduction. Figure 1 shows a few recombinant and diploid strains with enhanced performance over that of the parents. The recombinants presented a wide range of performance. The greatest increase was detected in the diploid MP, which had a 50% increase in SCP production as compared to parent M, and a 30% increase in COD reduction as compared with parent P. We conclude that the genome interaction between the parents had more impact on the performance of the recombinants than on that of the diploids. This suggests that enhancement of both measured parameters is more easily obtained by the construction of diploids than by segregation. However, is important to consider that diploids are unstable and tend to segregate, which is undesirable in an industrial process. This condition can be stopped by the use of a

recessive lethal mutation. To determine if the increased performance of the diploids over that of the recombinants was due to the presence of multiple auxotrophic markers in the recombinants, we made a genetic comparison of the recombinants. No correlation was detected between the quantity of genetic markers and their performance.

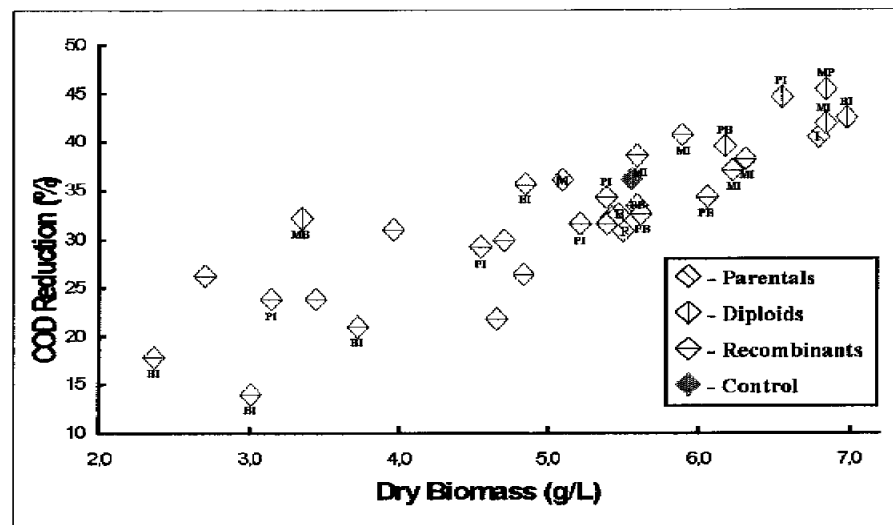


Figure 2. Dry Biomass Production and COD Reduction by *A. nidulans* Strains. Approximately 9×10^6 spores (4 replicates) were cultivated in 100mL of vinasse medium at 37°C with agitation at 150 rpm for 43 hours.

This study indicates that *A. nidulans* can be constructed to more optimally convert vinasse into biomass. *A. nidulans* can be used as a genetic model for the study of vinasse degradation. Using parasexual recombination, it was possible to increase the indices of pollution reduction, and of SCP production by the construction of diploid and recombinant strains.

Acknowledgment

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REACTOR DESIGN

OXYGENATION OF HYDROCARBONS BY PHOTOCATALYSIS: A GREEN ALTERNATIVE

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Abstract

The ability to develop an environmentally benign catalytic process for the partial oxidation of hydrocarbons has been the subject of intense investigation. The oxidation of hydrocarbons into their corresponding alcohols, aldehydes, ketones and if desired carboxylic acids would create an alternative production method for the highly sought oxygenates. The current research is directed towards the use of ultraviolet light with a specially prepared catalyst, titanium dioxide, for the selective oxidation of hydrocarbons. Synthesis of high-value organic compounds from linear, cyclic and aromatic hydrocarbons using photocatalytic oxidation with a semiconductor material, titanium dioxide (TiO₂), has been successful. Various hydrocarbons were partially oxygenated in both aqueous and gaseous phase photochemical reactors using ultraviolet light and titanium dioxide at mild conditions.

BACKGROUND

The partial oxidation of hydrocarbons by molecular oxygen, to form oxygenates which are further used as building blocks in the manufacturing of plastics and synthetic fibers, is an important process in the chemical industry. Current processes are energy intensive, have low conversion efficiencies and generate environmentally hazardous waste and by-products. In particular, autooxidation of small alkanes, alkenes, or aromatics is inherently unselective, whether conducted in the gas or liquid phase or catalyzed by transition metals. One major reason selectivities are low is the desired products (such as aldehydes or alcohols) are more easily oxidizable by O₂ than the parent hydrocarbon. Overoxidation can be minimized only by keeping conversions low, a serious disadvantage from a chemical processing standpoint. Therefore, a major challenge in this field is to find a reaction pathway that affords the primary product with high selectivity and a high conversion of the hydrocarbon.

MECHANISM

Over the past few years there has been considerable work aimed at using semiconductors as photocatalysts. Of particular interest to us has been the selective oxidation of hydrocarbons and aromatics to the corresponding oxygenates where TiO₂ functions as the photocatalyst. Titanium dioxide is biologically and chemically inert, stable with respect to photocorrosion and chemical corrosion, and an inexpensive catalyst. When the anatase form of TiO₂ is illuminated by UV light with wave lengths below ~390 nm, absorption of the light within the solid allows excitation of valence band electrons into the conduction band, leaving behind holes. The photogenerated holes are believed to have an oxidation potential of about 2.6V, therefore, possessing considerable oxidizing capability. If these electrons and holes can reach the surface of the catalyst, a reaction between species at the particle/solution interface can occur. The species to be oxidized is believed to adsorb on the surface of the particles to intercept the energetically favorable and rapid process of electron-hole recombination. Therefore, photochemical reactions at particle/solution interfaces are controlled by both relative redox energies and adsorption characteristics.

The photocatalytic oxidation of many organic molecules, including saturated hydrocarbons, by optically-excited semiconductor oxide is thermodynamically allowed in the presence of oxygen at room temperature. Selectivities different from those obtained by other oxidation means have been obtained with an acceptable quantum yield showing the potential of this method for syntheses.

EXPERIMENTAL

In this project we have been investigating the photochemical activity of TiO₂ as a low temperature alternative for chemical oxidation. Our efforts are directed to the use of heterogeneous gas and liquid phase reactors for the partial oxidation of alkanes and olefins to alcohols, aldehydes and ketones.

Liquid Phase Reactions

Oxidations of hydrocarbons performed in an aqueous environment have shown the dependence of the reaction on pH, catalyst loading, temperature, oxygen concentration, water-to-organic substrate ratio and light intensity.

Aqueous phase photooxidation of hydrocarbons using a batch reactor for 2 hrs showed high initial conversion rates (of 20-35 %) to respective alcohols and aldehydes. The selectivity decreased at longer reaction times due to over-oxidation to ketone and carboxylic products. Aliphatic compounds were produced from ring compounds, such as cyclohexane, as the result of overoxidation and hydrolysis. Aqueous phase reactions also encounter separation problems. To address this, we are also studying the catalytic activity of TiO_2 immobilized on polymeric matrix.

Gas Phase Reactions

Gas phase photocatalytic oxidation reactions of hydrocarbons were performed by flowing a known mixture of heated humid air with the organic vapor through an annular reactor. The efficacy with which the photoreactor operates may be influenced by the oxygen concentration, the light illumination, the properties of the photocatalytic coating, and the conditions within the fluid phase affecting contact of the substrate to the TiO_2 surface. Gas phase reactions eliminate the separation step and minimize the adsorption problem; they also allow better control of the temperature, humidity, composition of the reactants and contact time. Substrates investigated, experimental conditions and products formed are shown in Table 1.

Using the system shown in Figure 1, photocatalytic oxidations of toluene with air, flowing at 1 ml/min and 2 l/min respectively, at 150°C with 450W UV source, showed overall conversion of 15% per pass with 85% selectivity to benzaldehyde. Experiments with cyclohexane have demonstrated the production of cyclohexanol, cyclohexanone as major products. A conversion of 45% per pass based on cyclohexane disappearance was achieved at high oxygen concentrations. From the oxidation of n-pentane products resulting from the oxidation of the secondary carbon were the main products detected. Oxygen concentration and water vapor content dramatically affect the conversion and yield of the reactions. Variables that are also important but are less critical in affecting selectivity and yield include temperatures, flow rates, catalyst support and reactor design. The use of nano-structured and/or metal doped TiO_2 helped to increase the catalyst activity and possible use of visible light for the process. Research in this area could lead the use of solar energy and air for photooxidation of organics.

Figure 1. Schematics of Gas phase Photooxidation Process

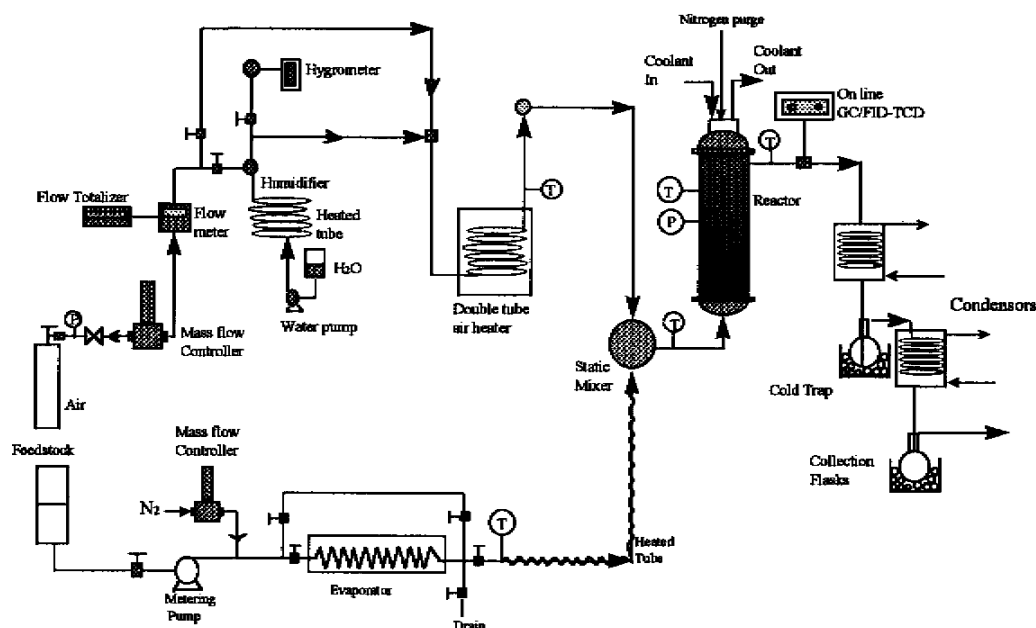


Table 1. Photocatalytic oxidation of hydrocarbons on TiO₂ film

Substrate	Conditions	Time of illumination	Products
Cyclohexane	150°C, under air	10 - 70 sec	cyclohexanone cyclohexanol
Toluene	150°C, under air	10 - 70 sec	benzyl alcohol benzaldehyde benzoic acid
Methylcyclohexane	150°C, under air	10 - 70 sec	methylcyclohexanone* 3-methyl-2-cyclohexen-1-one methylcyclohexol*
n-pentane	150°C, under air	10 - 70 sec	2-pentanol 2-pentanone 1-pentanol

*2,3,4 isomers

METHANE REFORMING WITH CARBON DIOXIDE: COMPARISON OF A FIXED BED REACTOR WITH A MEMBRANE REACTOR

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Summary

Methane reforming with carbon dioxide was studied on supported Ni and Rh catalysts at atmospheric pressure in the temperature range 898-1023 K. Experiments were conducted in a fixed bed reactor and a membrane reactor. The Ni and Rh catalysts provided methane conversions close to thermodynamic levels without any deactivation in the fixed bed mode of operation. The membrane reactor incorporated porous Vycor glass and modified Vycor glass as membrane materials and methane conversions were higher than in the fixed bed reactor.

Introduction

Many investigators¹⁻¹⁰ have focused on the development of reforming catalysts which show high activity towards syngas formation. However, most have reported rapid catalyst deactivation due to carbon deposition (coking). Also, the conversion of methane by reforming with carbon dioxide is limited by thermodynamic equilibrium. Equilibrium conversions in such reactions can be overcome by the preferential removal of one of the products of the reaction. In recent years, membrane reactors have become increasingly popular to combine reaction and separation and thereby overcome equilibrium limitations. Several researchers¹¹⁻¹⁴ used membrane reactors for various applications and reported improved performance as compared to fixed bed reactors. Our research focused on the development of active and stable catalysts for the methane reforming reaction. It also involved the testing of commercially available membranes and the development of lab modified membranes to selectively remove hydrogen and thereby provide higher conversions of methane.

Results and Discussion

We have developed supported Ni and Rh catalysts that were resistant to coking and exhibited stable operation for tens of hours of operation. These catalysts were also highly active and provided conversions close to equilibrium conversions between 898 - 1023 K. The Vycor membrane had an average pore size of 40 Å and the mode of separation of all species was predominantly by Knudsen diffusion. The membrane reactor configuration improved methane conversion considerably as compared to the fixed bed configuration. Experiments conducted with the modified membrane provided higher conversions of methane as compared to the Vycor membrane

reactor. The modified membrane exhibited high selectivity to hydrogen. Elemental analysis of fresh and spent catalyst samples did not indicate any significant coking.

Conclusions

Stable and active supported Ni and Rh catalysts were developed for the methane reforming reaction. Significant improvements over equilibrium conversion was achieved by the use of the membrane mode of operation. The new modified porous glass membrane developed in the laboratory exhibited high selectivity to hydrogen.

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NEW REACTOR DESIGNS FOR MINIMIZATION OF WASTE BYPRODUCTS AND PERFORMANCE OPTIMIZATION

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ABSTRACT

Reactor design has been traditionally based on steady-state operation mode. However, such design is not always optimum, for example due to catalyst deactivation or low selectivity. One such class of reactions involves oxidation catalysis, and in particular the oxidative coupling of methane to ethylene and ethane. Current technology for methane utilization is based on steam reforming. The available process is endothermic and about half of the methane is utilized for heating, resulting in significant energy loss and unacceptable pollutant emissions of carbon dioxide (green house effect).

In this work, we explore new reactor designs based on dynamic operation modes of microreactors for optimization of reactor performance and significant reduction of waste byproducts at the source. We combine state-of-the-art experimentation with detailed mathematical modeling. Results are contrasted for co-fed methane/oxygen mixtures as well as periodic alternating feeding of reactants using various oxide catalysts. Continuous catalyst regeneration and reactor scale up issues will be also discussed.

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HETEROGENEOUS CATALYSIS

DEVELOPMENT OF HETEROGENEOUS ALDOL CONDENSATION CATALYSTS

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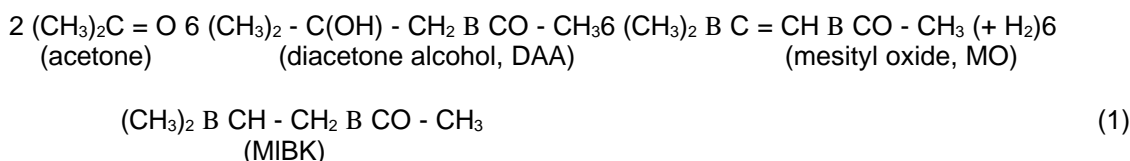
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Introduction

The development of solid catalysts to replace homogeneous catalysts in commercial chemical processes is the subject of intense research. For a wide range of processes, replacing aqueous homogeneous catalysts with solid catalysts *eliminates* waste streams that are costly to control. One example of interest is the self-condensation of acetone and related compounds. This process is practiced industrially using homogeneous liquid base catalysts, such as sodium and calcium hydroxide. Over 2 billion pounds of these products (methyl isobutyl ketone [MIBK], crotonaldehyde, and 2-ethyl hexanol) are produced in the United States each year¹. Liquid base catalysis generates a wastewater stream that must be neutralized and disposed, at significant cost. There is a clear economic and environmental driving force to develop *heterogeneous* catalysts to replace the current homogeneous catalysts², eliminating this byproduct stream.

Objective

The objective of the current research is to develop an understanding of the self-condensation and hydrogenation reactions of acetone on heterogeneous catalysts. The reaction of interest here is the condensation of acetone and its subsequent hydrogenation to MIBK:



The condensation of acetone to MO is thermodynamically limited to 20% conversion at the conditions of interest here (378 K), but the overall reaction from acetone to MIBK is not thermodynamically limited. The acetone-to-DAA reaction is base-catalyzed, the DAA-to-MO reaction is acid-catalyzed, and the final hydrogenation step requires a metal.

Experimental

The acetone to MIBK reaction was studied on a series of catalysts containing acid/base sites as well as supported metals for hydrogenation of MO to MIBK. The reaction studies were carried out in a 50 cm³ micro-Robinson batch reactor for 4 hours in duration at 120 °C and 350 psig with hydrogen supplied to the headspace to maintain constant pressure.

Results and Discussion

The batch reactor studies showed the following:

Catalyst	Acetone conv., %	Diacetone alcohol	Mesityl oxide	Selectivities		
				MIBK	Iso- propanol	Other products ^a
Blank run	3.14	0	0	0	>99	0
10%Ni/ -Al ₂ O ₃	20.3	26.9	63.1	8.71	0	0
10% Ni/Nb ₂ O ₅	10.9	5.36	81.7	12.9	0	0
5%Pd/ -Al ₂ O ₃	7.85	13.1	52.1	34.8	0	0
5%Pd/ZrP	9.5	9.85	67.8	20.8	0	1.52
0.7% Pd/ZSM-5	13.7	4.22	77.5	18.3	0	0

^aThe only products observed in this case were di-isobutyl ketone and 2-heptanol.

The reaction appears to proceed via the sequential condensation, dehydration, and hydrogenation sequence (reaction¹). There is no evidence for the formation of MIBK by cross-condensation of isopropanol (which could be

formed by direct acetone hydrogenation) and acetone. Only the Pd/ZrP catalyst³ showed any activity for the further conversion of MIBK. There are distinct differences among the catalysts, with the Pd catalysts showing more selectivity for MO hydrogenation than corresponding Ni catalysts. The Pd catalysts preferentially hydrogenate the desired C=C double bond in MO rather than the C=O bond⁴, forming the desired product MIBK rather than the alcohol.

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NEW EFFICIENT, SELECTIVE, TOTALLY CHLORINE FREE WOOD PULP BLEACHING TECHNOLOGY

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A new totally chlorine free (TCF) bleaching technology will be described in which hydrogen peroxide is activated catalytically to rapidly delignify and bleach kraft wood pulp under mild conditions in basic water. The process employs easily-prepared iron catalysts containing nontoxic elements that, by virtue of the ligand design strategy employed to produce them, are long-lived under operating conditions. Bleaching proceeds rapidly at micromolar catalyst concentrations from room temperature to 50 °C to deliver superior selectivity for lignin over cellulose oxidation compared to conventional TCF processes employing hydrogen peroxide, oxygen, or ozone. The hydrogen peroxide is used efficiently in the new process. For example, at 50 °C with a charge of 4% H₂O₂ on oven-dried pulp, significant delignification (kappa number 21.5 to 12.5) is achieved in a 75 minute bleaching cycle without the chelation pretreatments common to existing peroxide processes; the viscosity change is 41.5 to 32 mPa.s). These and other factors indicate that the new technology, called ~PFe~technology, possesses significant environmental and technological advantages over all currently existing TCF technologies.

A NEW CATALYTIC, SELECTIVE, AEROBIC TECHNOLOGY TO CONVERT WOOD TO PAPER

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ABSTRACT

A new liquid-effluent free technology for the delignification of wood or wood pulp has been developed using early-transition-metal oxygen-anion clusters (polyoxometalates or POMs). The POMs perform two separate functions: (1) the selective delignification of wood pulp, and (2) the catalytic mineralization (wet-air oxidation using dioxygen) of all the organic waste from the delignification step. These two steps sum to a net chlorine-free, liquid-effluent free, catalytic technology for the conversion of wood pulp (lignin and cellulose) to cellulose ready for paper manufacture. In addition, this green technology, which embodies a new approach to selective catalytic oxidation by dioxygen, provides new opportunities for more conservative utilization of changing forest resources.

INTRODUCTION

Wood-pulp manufacturers worldwide face formidable technical challenges in their efforts to develop more environmentally sustainable methods for removing lignin from wood pulps. The long term goal of these efforts is to develop the technology necessary for the operation of effluent free mills. Moreover, in the northern hemisphere, where high quality forest resources are becoming less readily available, there is an additional need for versatile technologies capable of producing high-grade chemical pulps from increasingly heterogeneous wood feedstocks. The process herein described—the result of a collaboration between the U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, the Emory University, Department of Chemistry and the University of Wisconsin-Madison, Department of Chemical Engineering—was designed to meet these challenges.

Wood. Wood is a composite material, highly organized at the cellular and molecular levels. It consists primarily of carbohydrates (cellulose and some hemicelluloses) and lignin¹. Lignin, which constitutes roughly 20-35% by weight of most woods, is a complex polymer formed by oxidative polymerization of phenylpropane derivatives. Cell division and growth are limited to the cambium layer at the outer circumference of a tree. Upon maturation, wood cells die, leaving behind rigid cell walls (wood fibers) constructed of lamellar layers of carbohydrate polymers. Lignin is found both within the cell walls and as a "glue" binding the fibers together. In the manufacture of paper, individual fibers are separated from one another in a pulping process and then bleached. The bleached wood pulps are suspended in water and formed into thin sheets.

Wood pulp. Pulps can be made in two ways, either by mechanical separation of wood fibers (mechanical pulps) or by chemical removal of lignin (chemical pulps). The amount of lignin remaining in the pulp affects both the strength and chemical stability of the finished paper. Mechanical pulping results in fiber degradation and leaves a high level of residual lignin. These pulps are used for the manufacture of lower quality paper and newsprint. The "yellowing" that occurs upon exposure of these products to light arises from photochemical changes in the lignin component of the paper. Chemical pulps, used to manufacture high quality paper products, are often produced by cooking wood chips in water solutions of alkaline sulfide (Na₂S; kraft pulping). During kraft pulping, most (but not all) of the lignin is removed. In addition, reactions of lignin and some carbohydrates with sulfide give rise to highly colored conjugated aromatic structures. The purpose of bleaching is to degrade and remove these chromophores along with residual lignin.

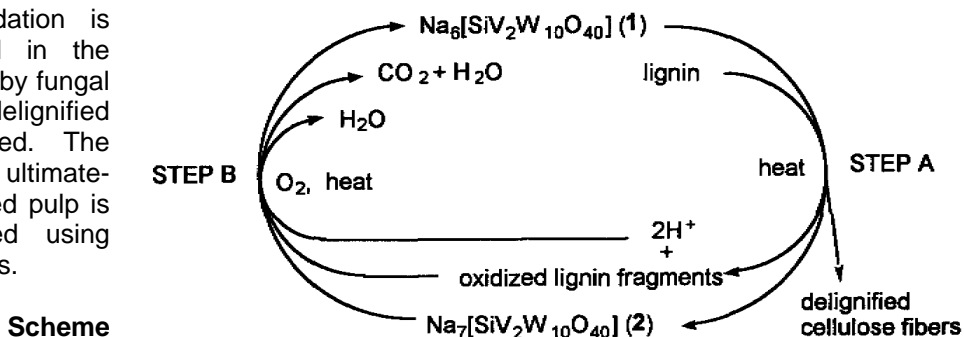
Bleaching. In the past, bleaching was widely carried out using elemental chlorine (Cl_2). However, reactions of Cl_2 with conjugated aromatic structures and residual lignin in the pulp generate chlorinated aromatic compounds that possess a range of toxicological profiles. As a response, U.S. manufacturers are replacing Cl_2 with chlorine dioxide (ClO_2), or with combinations of ClO_2 , dioxygen (O_2) and hydrogen peroxide (H_2O_2). Doing so will enable U.S. manufacturers to meet regulations recently promulgated by the Environmental Protection Agency that sharply limit the amount of chlorinated organic compounds that may be released to biological waste-treatment facilities. Looking ahead, totally effluent- or chlorine-free process are an attractive prospect, as is the development of more versatile and higher-yield pulping methods.

At present, no pulping method exceeds the kraft process in effectiveness and cost. And, despite world-wide efforts to develop alternatives, none match Cl_2 and ClO_2 in cost and effectiveness. Oxygen, the most obvious option, is not sufficiently selective. Due to uncontrolled radical-chain autoxidation reactions, cellulose fibers suffer severe oxidative damage when O_2 is used to remove more than modest amounts of residual lignin. Although a good brightening agent, hydrogen peroxide, the next most attractive candidate, is only mildly effective at removing lignin. While ozone (O_3)—a third oxygen-based oxidant—readily oxidizes lignin, it also reacts rapidly with cellulose fibers. Complex reactors have been designed to minimize cellulose damage by increasing the rate of diffusion of gaseous O_3 into wood-fiber walls. Nonetheless, the poor selectivity of O_3 has hindered its acceptance by industry and places distinct limits on its versatility.

DELIGNIFICATION USING POLYOXOMETALATES AND OXYGEN

A new strategy for selective delignification of wood or wood pulp by oxygen in water, the most environmentally compatible and least expensive oxidant and solvent, is herein reported². Several long-standing obstacles to the development of such systems are addressed using equilibrium solutions of a transition-metal oxygen-anion cluster (polyoxometalate or POM)³ of formula $\text{Na}_6[\text{SiV}^{\text{V}}_2\text{W}_{10}\text{O}_{40}]$ (**1**). Equilibrium solutions of **1** are obtained by preparing the target Keggin anions from their component oxides (i.e., SiO_3^{2-} , VO_3^- and WO_4^{2-}) under conditions similar to those required for their use in catalysis. The equilibrium catalyst systems thus obtained possess a number of functions and attributes, several unprecedented: (1) O_2 is the only oxidant used. (2) Water is the only solvent required. (3) Unlike coordination or organometallic compounds that possess organic ligands, **1** is thermodynamically stable toward oxidative degradation. (4) The catalytically active species, **1** is in equilibrium with its synthetic precursors under operation conditions, a rare situation in catalysis. Because the catalyst is thermodynamically stable, it is remarkably robust; should it be degraded during reaction, its optimal form is spontaneously reconstituted. (5) The catalyst system (**1**), its precursors and other species (present at equilibrium) functions as its own pH buffer.

The delignification process is designed to be effluent free. As such, the polyoxometalate carries out two distinct functions, anaerobic delignification in step A and wet oxidation (mineralization) of dissolved lignin fragments in step B (Scheme). In step A the wood pulp is treated under anaerobic conditions with the fully oxidized catalyst, **1**. Specifically, a slurry (0.01 g pulp/mL solution) of unbleached softwood kraft pulp fibers in an aqueous 0.2 M equilibrated solution of **1** is held at 150 °C for three hours under argon. In this step, the lignin is oxidized by the POM forming $\text{Na}_7[\text{SiV}^{\text{IV}}\text{V}^{\text{V}}\text{W}_{10}\text{O}_{40}]$ (**2**, the one-electron reduced analog of **1**) and products derived from lignin oxidation and depolymerization. The mechanism of lignin degradation is analogous to that observed in the biological degradation of lignin by fungal enzymes⁴. After step A, the delignified cellulose fibers are collected. The viscosity, an index of fiber and ultimately paper strength, of the treated pulp is comparable to that obtained using traditional Cl_2 and ClO_2 methods.



In step B, O_2 (2 MPa) is added to the catalyst solution that now contains dissolved lignin fragments and reduced POM, **2**, and the system is heated to 210 °C for 3 hours. The POMs present catalyze the oxidative mineralization (wet oxidation) of the dissolved lignin fragments to CO_2 and H_2O . Concurrently, **2** is reoxidized to **1**. Steps A and B thus sum to the selective removal and oxidative mineralization of lignin by O_2 and **1**.

Because the β -D-glucopyranoside linkages in cellulose are hydrolyzed in acidic media, step A must be carried out at neutral or higher pH using a suitable buffer, without which, cellulose degradation would be difficult to avoid. At the same time, Step B necessarily involves the consumption of H^+ ions, such that the H^+ content of the system is unchanged by a full cycle (steps A and B). In the POM system reported here, the H^+ ions generated in step A and the OH^- anions generated in step B are rapidly consumed by reversible reactions of the metalate species present in equilibrium with POMs **1** and **2**. More specifically, the H^+ ions are consumed in condensation reactions and the OH^- anions are consumed in hydrolysis reactions. In addition to **1** and **2**, the dominant species present in steps A and B are WO_4^{2-} , $cis-[V_2W_{40}O_{19}]^{4-}$ and $\alpha-[SiVW_{11}O_{40}]^{5-}$ whose concentrations can be quantified by ^{183}W NMR and ^{51}V NMR.

The stability and unique self-buffering capacity of this POM-based catalytic delignification system permit continuous operation. As a model for sustained industrial operation, steps A and B were repeated sequentially 10 times. Six key features remained unchanged throughout the 10 cycles: (1) the concentration of **1** reduced during delignification; (2) the drop in lignin content of the pulp; (3) the concentration of **2** reoxidized by O_2 ; (4) the quantity of CO_2 evolved; (5) the pH of the POM solution; (6) the distributions of POMs present as quantified by NMR. The constancy observed in these parameters lends strong support to the argument that the POM system is thermodynamically stable, an important requirement for sustained operation.

SUMMARY

We have described a new technology for the delignification of wood or wood pulp that is green in several diverse ways: it is free of chlorine and organic additives, selective, catalytic and uses only O_2 and H_2O . It is also flexible, robust and represents an innovative method for selective catalytic oxidation by O_2 . A pilot plant trial of the first prototype POM bleaching system is being planned. Moreover, recent trials have shown that POMs might make it possible to increase the yield and versatility of pulping processes while eliminating the need for sulfide and the associated formation of volatile organosulfur compounds.

Acknowledgments

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ALTERNATIVE SOLVENTS

THE GREENING OF A FUNDAMENTAL REACTION IN ORGANIC CHEMISTRY

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An important step in the history of modern chemistry was the introduction of magnesium for carbon-carbon bond formations¹ by Barbier and Grignard about a century ago,² through the addition of an organometallic reagent to a carbonyl group. The study of magnesium-based reactions since then has sparked the development of new reagents based on electronically more negative and more positive metals as well as semi-metallic elements for various synthetic purposes to tailor reactivities and selectivities (chemo, regio and stereo).³ For carbonyl additions based on organomagnesium reagents, it is generally accepted that strict anhydrous reaction conditions are required for a smooth reaction.⁴ The presence of moisture inhibits the reaction. Various methods, such as using dibromoethane⁵ or iodine initiators, mechanical activation⁶ and ultrasonic irradiations,⁷ have been developed to help initiate the reaction. More recently activated magnesium has also been developed.⁸ Because of economical and environmental concerns, the use of water as a solvent for metal-mediated carbon-carbon bond formations has generated considerable interests. Within the last several years, various metals have been developed to mediate Barbier-Grignard type reactions.⁹ For a long time, we have been intrigued by the possibility of performing classical Barbier-Grignard reactions by using magnesium in water. The study would possibly extend the scope of aqueous metal reactions as well as increase the understanding of the mechanism of the classical Barbier-Grignard reaction. However, in view of the high reactivity of organomagnesium reagents toward water, it is doubtful that magnesium could be used for such a purpose. Nevertheless, this question has constantly haunted our minds and led us to test the magnesium-mediated allylation reaction of benzaldehyde in water. Historically, the allylation of carbonyl compounds with allylmagnesium reagents had not been well-established for decades until Gilman and McGlumphy developed a new procedure to prepare Grignard reagents from allyl halides.¹⁰ Herein we report the observation that Barbier-Grignard allylation of aldehydes (**1**) with magnesium and allyl halides (**2**) proceeds smoothly in water (Eq. 1).

To start our investigation, we reacted allyl bromide with benzaldehyde and magnesium turnings in 0.1 N aqueous HCl for 3 hr at room temperature. TLC analysis of the ether extract clearly showed a spot that corresponds to the desired allylation product. Subsequently, ¹H NMR measurement of the crude reaction mixture showed about 28% of the allylation product (**3**), together with 66% of the pinacol coupling product (**4**),¹¹ and 6% benzyl alcohol. This promising result prompted us to examine factors that influence the reaction. We then examined in greater detail the effect of the solvent system on the magnesium reaction by using various combinations of water and THF as the reaction solvent together with a small amount of iodine to initiate the reaction. Work up of the reactions involved extraction with diethyl ether, drying over magnesium sulfate, and careful removal of the low boiling solvent in vacuo. In the case where no organic co-solvent was involved, the reaction mixture was extracted with CDCl₃ and the extract was examined directly. ¹H NMR spectra of the reaction products under various solvent combinations revealed a very interesting phenomenon. The results are listed in Table 1. In freshly distilled THF dried over sodium/benzophenone, the reaction between benzaldehyde, allyl bromide and magnesium turnings together with a small amount of iodine occurred almost quantitatively, generating the expected allylation product. The addition of a small amount of water to the freshly dried THF did not affect the progress of the reaction. The expected reaction proceeded effectively until about 7% of water in THF was used, which suddenly blocked the reaction progress. After repeating several times, we identified a mid-point (entry 4) at which ca. 56% conversion of the starting benzaldehyde was observed. However, when the composition of the solvent is changed to water alone, a smooth reaction started again, generating the allylation product albeit with a low conversion. The low conversion could be attributed to the formation of magnesium hydroxide on the metal surface which blocks further reactions. Additional reactions using 0.1 N HCl or NH₄Cl solutions as the reaction solvent gave a quantitative conversion, generating a mixture of the allylation and pinacol coupling products. Other aromatic aldehydes gave similar results; whereas reactions of aliphatic aldehydes gave more complicated mixtures. The use of 0.1 N NH₄Cl aqueous solution as the solvent was found to be superior to the use of 0.1 N HCl. The use of a catalytic amount of InCl₃ did not affect the reaction.¹² Changing the allyl bromide to allyl iodide further increased the formation of the allylation product (58%). Only a minute amount of the allylation product was observed with allyl chloride. In the absence of HCl, NH₄Cl or iodine, virtually no reaction was observed with allyl bromide. Experiments revealed that, with iodine, the reaction of allyl bromide proceeded through an allyl iodide intermediate. The formation of such an allyl iodide intermediate, however, is not necessary in 0.1 N NH₄Cl or 0.1 N HCl.

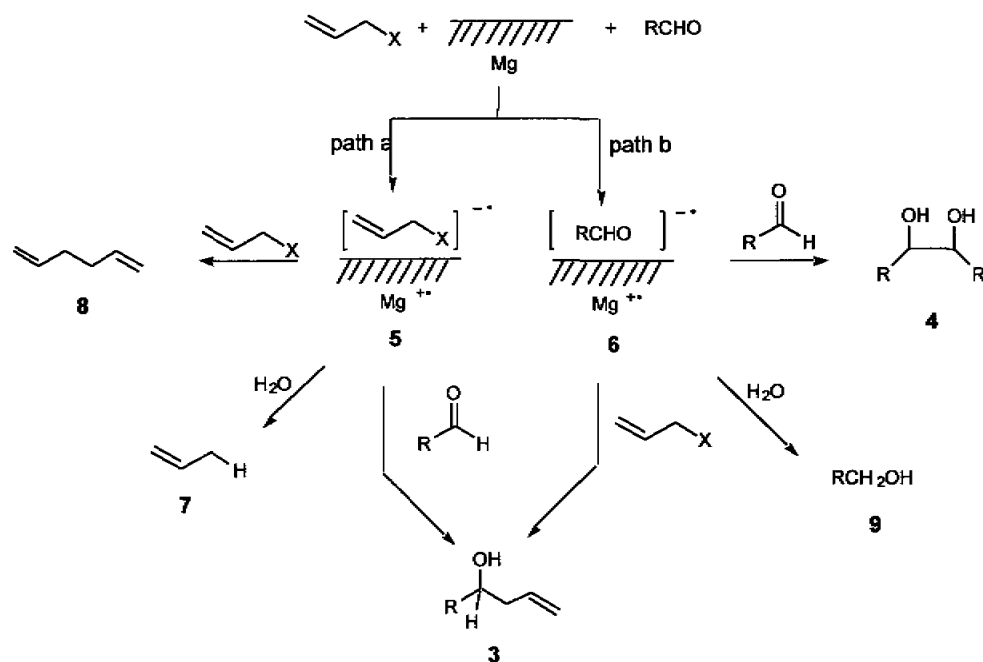
To explain the unusual phenomenon of the solvent change, we postulate that in freshly dried THF, the normal

reaction occurs between the organo halide and magnesium generating the magnesium reagent. Subsequent reaction with carbonyl compounds generates the allylation product. However, in a homogeneous mixture of THF and water, the water molecule would be evenly distributed throughout the solution; hence the contact between water and the metal surface would prohibit the formation of the organomagnesium reagent. The solvent system with ca. 7% water may correspond to the point where the surface is completely covered by water molecules. With water alone, allyl bromide might be squeezed on to the metal surface due to hydrophobic effect;¹³ locally and microscopically, magnesium would not be in direct contact with water. The formation of allylmagnesium can thus occur as in dry organic solvents, which leads to the generation of allylation products.

The mechanisms of magnesium mediated Barbier and Grignard reactions have been studied intensively by several groups.^{14,15} It is generally believed that radicals on the metal surface are involved in the organomagnesium reagent formation reaction.¹⁴ There is still no conclusion as to the freedom of these free radicals.¹⁵ In order to gain mechanistic information of the present reaction, we quenched the allylation process in 0.1 N aqueous NH_4Cl . The reaction mixture was extracted with CDCl_3 and ^1H NMR spectrum was taken directly. The measurement shows the formation of the three products (allylation, pinacol, and benzyl alcohol) reflecting our previous experiments. In addition, 1,5-hexadiene was clearly formed. However, no propene formation was detected with NMR.¹⁶ In order to explain the experimental observations, we tentatively proposed Scheme 1. The transfer of electrons from magnesium to either the allyl halide (path a), or the aldehyde (path b), or both, generates the corresponding radical anions **5** and **6**. Then, reaction of either **5** with the aldehyde, or **6** with the allyl halide generates the corresponding allylation product **3**. Reaction of **5** with the allyl halide gives the Wurtz-coupling product **8**; reaction of **6** with the aldehyde gives pinacol product **4**. The reaction of these radical anions with water led to the corresponding reduced products **7** and **9**. Subsequent experiments show that in the absence of the allyl halide, the corresponding pinacol coupling product **4** was obtained.

Alternatively, the reaction of allyl bromide on the metal surface generates an organometallic intermediate which is in an equilibrium with the charge separated form and the radical form as proposed by Alexander.¹⁷ These two forms will also lead to either the protonation of the carbanion (overall reduction of the halide) or Wurtz-type

coupling;¹⁹ whereas the intermediate reacts with aldehydes through usual six-membered ring mechanism as proposed by Young and Roberts¹⁹ (represented by the symbol $\text{S}_{\text{E}}2'$).²⁰ The radical intermediate leads to the formation of 1,6-hexadiene, pinacol product and benzyl alcohol.²¹ A detailed exploration of the origin and synthetic utilities of this magnesium mediated reaction are under investigation.



Scheme 1. Postulated rationale for magnesium mediated carbon-carbon bond formation in water

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Example Experimental Procedure for the Magnesium Mediated Reaction in Water:

To a mixture of benzaldehyde (200 mg, 1.89 mmol), allyl iodide (950 mg, 3x1.89 mmol) in 0.1 N aqueous NH_4Cl (10 mL) was added magnesium turnings (1 g, 41.6 mmol). The mixture was stirred at room temperature for 12 h. The reaction was quenched by 1 N aqueous HCl and extracted with CDCl_3 . The extract was dried briefly over magnesium sulfate and a ^1H NMR spectrum was taken. Analysis of the ^1H NMR spectrum gives benzaldehyde (0%), the allylation product (58%), the pinacol coupling product (34%), and benzyl alcohol (8%).

THE DESIGN OF TECHNOLOGICALLY EFFECTIVE AND ENVIRONMENTALLY BENIGN SOLVENT SUBSTITUTES

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ABSTRACT

There is presently considerable interest in finding environmentally benign replacement solvents that can perform in many different applications as solvents normally do. This requires solvents with desirable properties, e.g., solvent ability, and without other undesirable properties, e.g., toxicity. This complex problem can be simplified because the behavior of solvents in all applications is governed by universal mathematical expressions. The identity of the solvent in these expressions is represented by coefficients, e.g., viscosity, activity coefficients. We have addressed the solvent design problem by using property prediction and phase equilibrium analysis methods in a computer algorithm to design mixtures with specific properties. We present a classification of the necessary properties for solvent design. The categories include general, dynamic, and equilibrium properties, environmental requirements, e.g., a VOC index, and performance requirements. These concepts form the basis of the PARIS II solvent design software which is near commercialization and which will also be presented.

INTRODUCTION

There are two principal approaches to replace environmentally undesirable solvents: (1) finding alternative technologies that do not use solvents and (2) finding alternative solvents. Finding alternative solvents is preferable because it uses existing processes with minor or no modifications. Unfortunately, the solvent substitution approach presents a serious technical challenges because one must design substitute solvents which are as effective as current solvents but have better environmental properties such as toxicity. There are a number of research efforts in the design of environmentally benign solvents that can be roughly classified into three categories: (1) screening the available solvent databases for single chemical substitutes, which includes the Solvent Substitution for Pollution Prevention (Joback, 1994), the Solvent Database Software Program (Hermansen, 1993), the Tool for Systematic Solvent Screening for Batch-Process Development and Revamping (Modi and Stephanopoulos, 1996), (2) designing new chemicals that meet specified requirements, which includes Molecular Design of Solvents for Liquid Extraction based on UNIFAC (Gani and Brignole, 1983), Designing Molecules Possessing Desired Physical Property Values (Joback and Stephanopoulos, 1990), Computer-Aided Molecular Design by Group Contribution (Nielsen and Gani, 1990), Group Contribution Approach to Computer Aided Molecular Design (Gani et al., 1991), Design of Optimal Solvents for Liquid-Liquid Extraction and Gas Absorption Processes (Macchitto et al., 1990), Computer-Aided Molecular Design of Solvents for Separation Processes (Pretel et al., 1994), and Design of Environmentally Safe Refrigerants Using Mathematical Programming (Duvedi et al., 1996), and (3) designing mixture replacements if no single chemical replacements are found or available, which includes Solvent Selection by Computers (Hansen, 1973), Computer Aided Mixture Design with Specified Property Constrains (Klein et al., 1992), Computer Program for Assisting the Design and Replacement of Environmentally Objectionable Solvents (Zhao et al., 1996), Computer Aided Solvent Substitution for Pollution Prevention (Cabezas et al., 1996), and Molecular Thermodynamics in the Design of Substitute Solvents (Zhao and Cabezas, 1998). For the first category, the main advantage is relative simplicity, and the disadvantage is that screening cannot always find substitutes because the information provided by the database is limited or because no existing chemicals can meet the requirements. For the second category, the main advantage is that it can design entirely new chemicals when no single chemical replacements are found or available, and the disadvantage is the increased complexity of molecular design. For the third category, the main advantage is ability tailor solvent properties precisely by using mixtures, and the disadvantage is the complexity of calculating and manipulating mixture properties.

The focus of this paper is the third category, designing mixture replacements. The objective of this paper is to discuss the concepts and ideas, which are important for the design of, substitute solvents including physical properties and environmental effects.

SOLVENT SUBSTITUTE DESIGN

In designing substitute solvents, one needs to match all solvent behavior including equilibrium and dynamic behavior, phase behavior, technical performance requirements, and environmental performance requirements. This is basically a mapping of the total behavior of one solvent into that of another in a space where the coordinates are physical properties and performance requirements constrained by phase behavior. For example, all the possible dynamic behavior of a solvent can be defined in terms of three modes of transport: momentum, energy, and mass. The simplest form of the transport expressions is Newton's law for momentum, Fourier's law for energy, and Fick's law for mass given by Eqs. 1-3 respectively.

$$t_{yx} = -\mu \frac{dv_x}{dy} \quad (1)$$

$$q_y = -\lambda \frac{dT}{dy} \quad (2)$$

$$J_{Ay} = -D_{AB} \frac{dC_x}{dy} \quad (3)$$

These three simple expressions plus momentum, energy, and mass balances can be used to derive general transport equations that can in principle represent solvent dynamic behavior in all possible uses or applications. The difference between one application and another depends on the initial and boundary conditions and other assumptions such as isothermal conditions that are imposed on the equations. There is an elaborate literature (Bird et al., 1960) in this area. What is important here is that in these three simple equations as well as in the more general transport expressions, the fluxes and driving forces do not depend on the individual components present, i.e., the form of these equations is independent of the particular chemical components present. The only place where the identity of the components appears is in the proportionality factors μ , k , and D_{AB} . For the more general expressions, other properties such as density, D , which are also characteristic properties of the individual components additionally appear. Therefore, if one matches the values of μ , k , D_{AB} , and D in one solvent to those in another solvent, then all the dynamic behavior of both solvents will be matched for any given application. This type of reasoning is also applicable to equilibrium behavior and to other solvent properties and requirements. For example, the most important expression in computing the static behavior of solvents is the fugacity expression of Eq. 4 below,

$$f_i^{(l)} = x_i \gamma_i f_i^o \quad i = 1, 2, \dots, n \quad (4)$$

where $f_i^{(l)}$ is the fugacity of component i in a liquid mixture, x_i is the mole fraction of a component x_i , γ_i is the activity coefficient of component i , and f_i^o is the reference fugacity of component i that can often be set equal to the vapor pressure, P_i^s . Again, the form of Eq. 4 is the same for all solvents, and the identity of the solvents appears only in γ_i and f_i^o or P_i^s . A general review of fluid physical properties and property prediction methods can be found in Reid et al. (1987).

In addition to matching bulk physical properties as already mentioned, it is also necessary to consider the activity coefficients to insure that the molecular interactions between the solutes and the solvent in the original and the substitute are generally similar. This insures that proposed substitute solvents will likely dissolve the same solutes and have similar effects to those of the original solvent. However, it is important to match only the activity coefficients of the solutes in the solvents at infinite dilution, i.e., zero solute concentration, so as not to include solute-solute interactions. Activity coefficients can be estimated from group contribution methods (Reid et al., 1987).

Lastly, it is also important to consider the environmental impacts of the solvent to be replaced and of the proposed substitute. The purpose is to formulate substitute solvents that have better environmental performance, i.e., lower toxicity, lower volatile organic emissions, etc. than the solvent being replaced. In the case of solvents, one needs to consider the inherent toxic effects of the solvent and the toxic effects due to volatile organic emissions separately. The reason is that when chemicals are mixed, their volatility changes due to the non-idealities in the mixture. Therefore, a chemical that has low risk by inhalation due to low volatility by itself can have a much higher volatility and a much higher risk when mixed with other chemicals, and this needs to be carefully considered.

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SOLVENTS IN THE PRACTICE OF GREEN CHEMISTRY

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ABSTRACT

At this time, there is no one source of information on the present state of the science of solvents appropriate for use in Green Chemistry. Simply stated, it is the aim of this talk is to introduce the use of Green Solvents throughout chemistry and to provide an invaluable perspective on solvents currently applicable in Green Chemistry. The talk will examine solvents in world chemical perspective. Highlights will include defining characteristics of Green Solvents, their current usage and their importance (ecologically and economically.) It discusses solvents in specific commercial and non-commercial practices. Discussions on actual solvents will serve as a starting point for further discussions on how these solvents can be found or made. The information will be authoritative, current, and documented.

INTRODUCTION

The science of chemistry has matured in numerous areas, which can be compared to the development of an art form. The current emphasis on pollution prevention has its expression in Green Chemistry through the creative uses and designs of chemicals. This necessarily involves the utilization of existing knowledge, wielded in a novel manner by the artist. Within this understanding, solvents are a necessary medium in this art.

Green Chemistry embraces the design, manufacture, and use of chemicals and chemical processes that have little or no pollution potential or environmental risk and are both economically and technologically feasible. This teleological view of Green Chemistry is counter to traditional expectations in chemistry. Chemists can not be ignorant nor can they claim to be unaware of the effects of the science in which we are engaged. Simply stated, Green Chemistry is the expression in chemistry for the global need for pollution prevention. It is the use of chemistry techniques and methodologies that will reduce or eliminate the use or generation of feedstocks, product, by-products, solvents, reagents, etc., that are hazardous to human health or the environment. It is important that chemists regard Green Chemistry affording new opportunities and possibilities in this science.

The goals and objectives of Green Chemistry will provide the chemist with a renewed vision for selecting appropriate chemistries. The deployment of solvents directly impacts the design of safer chemicals for use in research, industry and commerce. Modern day chemists are now expected to develop and to use chemical substances that are safe to human health and the environment as well. Green Chemistry principles become the guidelines, indeed the impetus, for scientists engaged in the discipline of chemistry.

The worldwide solvents market is estimated at over 30 billion pounds per year. In the face of this positive response to the pollution prevention mandate, pursuing environmentally sound strategies continues to be seen by a large cross section of scientists as detrimental to the principal goals of chemistry. Such a perception is anachronistic. This belief directly addressed by the appropriate use of solvents and the development of new, green solvents.

SUMMARY

Solvent use in chemistry is pervasive. In the emerging area of Green Chemistry careful reasoning must enter into the choice of solvents. Chemists use solvents for many reasons, but primarily they are used as reaction media, in separation/purification technologies and in cleaning technologies.

As a means to demonstrate the intimidating range of applications, we can look at three broad areas: Academic chemistry, industrial chemistry and "practical and ordinary chemistry". Green Solvents for Academic Chemistry would include early chemistries (Elementary through High School), organic, inorganic, biochemistry, medicinal, and teaching laboratories. Green Solvents for Industrial Chemistry would include solvents by industrial processes, health fields, analyses & special solvents, and military solvents. Finally Practical and Ordinary Chemistry would encompass household solvents, recreational solvents, transportation solvents, hygiene solvents, and food, cooking & nourishment solvents.

GREEN SOLVENTS

Solvents serve several roles in the world of chemistry. According to the end goal of Green Chemistry, the criteria for what determines a green solvent will vary, depending upon the use and ultimate fate of the solvent during the process. Likewise, the determination of what constitutes appropriate solvent usage in Green Chemistry might include any of the following actions: (i) redesign of the exact chemical nature of the solvent via synthesis, (ii) identification of equally useful but less toxic substitutes of another chemical class for use instead of a "traditional" solvent, or (iii) reducing/eliminating the use of Solvents for particular chemical processes. Understandably, therefore, the discussion of Green solvents will thread its way through forests of chemistry, ecology and philosophy. From the outset, the traditional considerations of synthesis yield (if we are dealing with reactions), perfect product recovery (separations) or commercial usefulness are no longer the only ones for a chemist during the choice of solvents.

What, then constitutes an appropriate solvent for Green Chemistry? Fundamentally, it must be a solvent which allows the chemist to accomplish his or her task, but in an environmentally conscious manner. The modern chemist is expected to consider environmental toxicity as part of the key elements affecting choice of solvents, so that they are minimally toxic to human health and the environment and disposed of in ways that do not contribute to pollution. The considerations for what constitutes a safe solvent might contain some of the following considerations:

- Must have reduced absorption;
- Environmental toxicity of it should be understood;
- Knowledge of its environmental fate is understood.

The environmental toxicology of a solvent is determined by many factors, such as bio-availability, metabolism, and the presence of structural features that may attenuate or enhance the reactivity of the parent molecule. Despite the structure-activity data available for many classes of commercial chemical substances, chemists have not recognized the use of structure-activity relations as a rational approach for choosing or designing new, less toxic commercial chemical substances, even though it can be an exceptionally powerful tool. With qualitative structure-activity relationships, the correlation of toxic effect and structure is made by comparing the structures of the substances in the series with corresponding effects on the toxicity. Through these, it may then be possible to predict a relationship between structure and toxicity and identify the least toxic members of a class of compounds as possible commercial alternatives to the more toxic substances.

In order to understand and to systematically categorize the solvents available to Green chemists, it is useful to utilize the historical classifications of solvents. The grouping of solvents into classes with common characteristics can be useful in focusing attention on features that may play a role in experimental solvent effects. Reichardt's review of classification schemes is thorough.

It is remarkable, that solvent classification, whether obtained through extensive empirical results or calculated entirely using statistical methods, correlates strongly with the chemist's intuition. This becomes the point of departure for green chemists, as the new direction of the science demand new properties to be incorporated into the art. These will include not only chemical properties, but safety properties, and environmental properties as well.

GREEN SOLVENTS: CRITERIA AND FUNCTIONS

The chemist who is able to recognize toxicophoric or toxicogenic substituents, or obtain information pertaining to a toxic mechanism, is in a much better position to judge the merits (according to the Green Chemistry paradigm) of particular solvent usage. The article by Stephen DeVito explains clearly the toxicological considerations for Chemists. Through the use of well-known toxicophoric or toxicogenic substituents, it might be possible to be alerted to the avoidance certain solvents or to the substitution of more friendly ones. There are instances, however, in which the toxicity of a substance is unknown and the toxic mechanism is not apparent or predictable from its structure; no obvious or known toxicophoric or toxicogenic substituents may be present. In this case the chemist will often need to conduct literature searches on the original substance to identify toxicity studies containing mechanistic information.

Toxicity considerations for choice of solvents include the degree of absorption reported in the literature, exploration of toxic mechanisms, and the use of Structure-Activity (toxicity) Relationships (SAR). The relative seriousness of the toxic effect depends upon the extent of exposure to the substance, its bioavailability, and the importance of the physiologic process that the substance has disrupted. Over this information must be laid the physical parameters of the solvent's use (i.e., amount, state, reaction environment, etc. But the utilization of these and the other approaches to design safer chemicals requires that the chemical designer has a basic understanding of the processes involved in chemical toxicokinetics and toxicodynamics. The response to the data acquired above may result in a new course of action, which might include identification of equally efficacious, less toxic chemical substitutes of another class.

To incorporate the Green Chemistry paradigm into a methodical framework, efforts must be expended in understanding the mechanisms of desired reactions (both existing and future), while simultaneously evaluating the steps and chemical components in terms of environmental cost/benefits. This *modus operandi* is novel and it has not been rigorously nor universally applied to the conscious design of new reactions. The development of new environmentally favorable routes for the chemical processes which span the breadth of chemistry is an area of considerable interest, whose importance will only expand as the pressures of the ecological movement are felt more. To achieve such a rigorous methodology which is applicable to the panorama of all chemical activities is certainly a monumental task, and it lies beyond the constraints of this chapter. However, in the balance of the material presented here, the path will be highlighted as it exists now and future possibilities will be indicated.

Table 1. Summary of general considerations in selecting a solvent

- I. "External" Considerations — Reduction of exposure or accessibility
 - A. Properties related to environmental distribution/dispersion
 - 1. volatility/density/melting point
 - 2. water solubility
 - 3. persistence/biodegradation
 - 4. conversion to biologically active substances.
 - 5. conversion to biologically inactive substances.
 - B. Properties related to uptake by organisms
 - 1. volatility
 - 2. lipophilicity
 - 3. molecular size
 - 4. degradation
 - C. Consideration of routes of absorption by man, animals or aquatic life
 - 1. skin/eyes
 - 2. lungs
 - 3. gastrointestinal tract
 - 4. gills or other species-specific routes
 - D. Reduction/elimination of impurities
 - 1. generation of impurities of different chemical classes
 - 2. presence of toxic homologs
 - 3. presence of toxic geometric, conformational or stereoisomers
- II. "Internal" Considerations — Solvent Performance
 - A. Facilitation of solution
 - 1. mechanistic understanding of solvated species
 - 2. condition of solution
 - 3. time scale
 - B. Reactivity of solvated species
 - 1. acceptable reactivity
 - 2. desired product
 - C. Avoidance of undesired side reactions
 - 1. mechanistic understanding of new media
 - 2. fine-tuning reaction

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SEPARATIONS

GREEN SEPARATION SCIENCE & TECHNOLOGY: USING ENVIRONMENTALLY BENIGN POLYMERS TO REPLACE VOCs IN INDUSTRIAL SCALE LIQUID/LIQUID SEPARATIONS

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One area of opportunity for new chemical science and engineering technology which will help meet the goals of Technology Vision 2020 is the development of new separations technologies that eliminate the use of flammable, toxic VOCs as solvents. Used in conjunction with, or instead of appropriate current manufacturing processes, such technologies would help to prevent pollution and increase safety. The long range goal of our research is thus to obviate the need for VOCs in many industrial separation and waste remediation technologies by the development of liquid/liquid separations utilizing benign polymers (e.g., polyethylene glycol). This presentation will discuss our study of aqueous biphasic systems and the emerging relationships between various polymer-based separations technologies currently under development to replace VOCs in industrial usage. We recently reviewed this area¹ and will present excerpts from that review here.

For the last several decades separations scientists have been employing the solubilizing properties of solutions of polymer molecules in aqueous solution to effect the extraction and fractionation of a wide variety of target solutes. Of particular interest in the context of our work are extraction systems variously referred to as, cloud point extraction (CPE)², micellar extraction (ME)³, aqueous biphasic systems (ABS)⁴, and extractions using thermoseparating polymers (TSP)⁵. There are some chromatographic methods such as micellar liquid chromatography, (MLC)⁶, micellar electrokinetic chromatography (MEKC)⁶, and admicellar chromatography⁷ to which we don't devote much attention here, but which, in our view, have many similarities. There are still other extraction techniques such as microemulsions⁸ and reverse micelles⁹ which we hardly consider at all simply because of the involvement of volatile organic compounds (VOCs).

Modern textbooks on solvent extraction may devote some small section to a consideration of the properties and applications of ABS, because of their importance in the biotechnology industry¹⁰, yet all of the aforementioned methods are recognizably variants of the liquid/liquid extraction technique. In fact, it is rare to find these techniques discussed simultaneously at all. There are over 70 volumes in the Surfactant Science Series¹¹ and yet only one covers the solubilizing properties of a wide range of these separations methods, and even that does not feature ABS¹². Another is devoted to block co-polymers of the oxy-alkalenes¹³ which, along with similar random copolymers, represent the major thermoseparating polymers. Yet despite the lack of common discussion, these novel micellar systems¹⁴ could feature in a discussion of ME systems, CPE systems, or TSP, whilst at the same time being obviously related to ABS.

It seems to us that all of these liquid/liquid extraction methods, each with its own, by now, quite vast and specialized literature, have as much in common as to distinguish them and are quite worthy of common consideration, especially in relation to the design of extraction and separation operations for industrial and environmental application. An extensive list of common features can easily be made including:

- All represent anisotropic or multiphase systems and thus lend themselves to development as solvent extraction systems.
- All may be applied to the solubilization of otherwise relatively insoluble hydrophobic species.
- None require VOCs for use in liquid/liquid extraction.
- All may be formed by addition of polymers to water.
- All of them may be said to rely on the structuring properties of liquid water for the formation of these heterogeneous multiphase systems and also, seemingly, for their solubilizing power.
- Very many of these techniques seem to depend on the remarkable properties of the poly(oxyalkylenes) and similar polymers, such as the poly(n-vinylpyrrolidones), to be effective.

The first two properties above allow these systems to be considered suitable for solvent extraction. The remaining properties listed above allow them to be considered as environmentally benign methods by the elimination of the requirement to employ VOCs. Indeed in the case of CPE and ME, application of these techniques is widely reported in the context of environmental remediation. The final point is related to the unusual solubility range of PEO in a variety of solvents and its ability to hydrogen bond to water molecules. It can

thus serve as the hydrophilic moiety in a wide range of block and random copolymers as well as nonionic surfactants¹⁵.

In order to attempt to redress this imbalance in the discussion of these systems, and to emphasize some of their common features, and hopefully to stimulate new thinking and avenues for research, the properties and features of some of these emerging liquid/liquid extraction technologies need to be discussed in a common forum. In the context of pollution prevention or environmental remediation applications, it may prove useful to be able to consider the similarities, differences, advantages, and limitations of what may be considered a "tool box" of environmentally benign polymer separations techniques (Figure 1) in order to take advantage of the wide range of opportunities in this area.

It has become somewhat traditional in all the fields covered here to stress the essential environmental benignness and toxicological safety of many of the polymeric biphasic and micellar systems reviewed. Also often emphasized is the bulk availability and cheapness of these materials. The reasons for the latter are not hard to find. As long ago as 1984 some 17 million metric tons of surfactant were being produced worldwide of which about two-thirds were anionics and one-third linear alkyl benzene sulfonates¹⁶. Presently some 500,000 tons of alkylphenol ethoxylates are produced annually¹⁷. These latter are produced mainly for use in detergents, paints, pesticides, textiles, petroleum recovery products, metal finishing fluids, and personal care products¹⁷; some 55% being used in industry, 30% in institutional cleaners, and the remainder in personal care products¹⁷. It has been said that some 0.7 billion kgs of alkyl ethoxylates are produced and released to the environment annually¹⁸. PEGs and their mono- and dicarboxylated forms constitute one of the most abundant classes of contaminants of natural waters¹⁸.

While it appears that modern surfactants are fairly readily biodegradable, and that indications of carcinogenicity, mutagenicity, and teratogenicity are lacking¹⁶, production of alkylphenol ethoxylates for household use in Europe is currently restricted on a voluntary basis and restrictions for industrial applications are expected by the year 2000 because of the reported toxic nature of the breakdown products of these materials¹⁷. They have additionally been suggested as nascent endocrine disrupters¹⁷.

In general, polyoxyethylenes and polyoxypropylenes and their copolymers have similar toxicity which is, in general, and in most studies very low, although aquatic toxicities in the mg/L range have been reported¹⁸. Some concern has been voiced as to their ability to transport and thus enhance the toxicity of other toxic materials, perhaps in analogy to the way in which similar materials may act as ionophores in relation to the cell membrane. Such is the current ubiquity of these materials in the environment, that it has even been suggested that polyoxyalkylene presence may be used as a diagnostic test for the existence of anthropic inputs into water courses¹⁷.

In view of the likely increasing constraints on the discharge of ethoxylated materials and the increasing pressure for complete plant closure, practical processes for environmental clean-up and large scale industrial application will have to recognize the requirement for the right choice of polymeric material at the outset. Innovative designs which limit discharges, prevent losses, and permit recycling will be at a premium.

CONCLUSIONS

All the liquid/liquid extraction techniques discussed above have many common features which convey challenges to the understanding of the underlying mechanisms and thus, in their utilization and in the design of practical separations processes. All form heterogeneous or phase separated solutions which lend themselves to the development of sophisticated separations methodologies, but most importantly, which utilize relatively benign media compared to conventional solvent extraction schemes. CPE utilizing solubilizing polymers and analogous solid phases developed for SPE (solid phase extraction, involving a porous particulate support) and SPME (solid phase microextraction, involving a membrane supporting phase) combined with MEKC represent opportunities to develop methods which dispense with the use of organic solvents in the analytical laboratory. Also, on the larger scale, each may be exploited to take advantage of subtle differences in solubility of target species which in many cases may be approached by a variety of methodologies. In some cases, polymers may be induced to undergo conformational or associational changes in response to environmental variables of which the most significant is temperature. The physico-chemical interactions of the relatively apolar phase may be manipulated to effect separations based on variable molecular properties of mixtures of molecules.

Currently, the greatest challenge lies in the development of wholly closed processes utilizing these materials.

Too much reliance has, in the past, been placed on their relatively benign nature. Increasingly, the relative sophistication of modern chemical synthetic procedures is leading to the production of a rapidly growing range of polymeric materials (reviewed in reference 15), having diverse properties and potential for useful application. It seems likely that separations processes based on these new synthetic polymers will develop at a rapid rate in the near future. To this end we look forward to seeing much more comparative physical and chemical data on these alternative solvent systems to allow direct comparison with traditional solvent extraction methods. Ultimately, one might envisage the development of a solvent replacement 'toolbox' from which the polymeric system best suited to a particular separations need could be quickly isolated.

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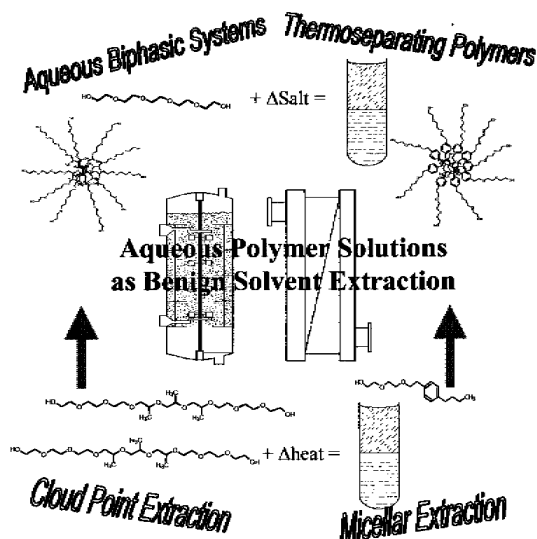
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Figure 1. A solvent replacement 'toolbox' can be envisioned from which the environmentally benign polymeric system best suited to a particular separations need could be quickly isolated.



EMISSION REDUCTION OF PERFLUOROCOMPOUNDS IN SEMICONDUCTOR MANUFACTURERS VIA CAPTURE AND RECYCLE

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ABSTRACT

Perfluorocompounds (PFC's), including SF₆, C₂F₆, CF₄, NF₃, CHF₃, and C₃F₈ are essential to many manufacturing processes in semiconductor industry. However, these gases are also classified as greenhouse gases; they are much more potent than carbon dioxide, due to their extremely long life time and strong absorption in radiation. Environmental scientists believe these gases may last as long as 50,000 years in the atmosphere. Over 1.6 million pounds of PFCs were used in 1995 in the US semiconductor industry, at an estimated cost of over 45 million dollars. This amount could be doubled by year 2000. The US government has responded to its international commitment (RIO Earth Summit '92 and Kyoto Protocol '97) by promoting reduction in PFC emissions in various industries.

The semiconductor industry has currently four options for addressing the emission reduction: 1) change the process chemistry by eliminating the usage of PFC, 2) improve the process efficiency in utilizing these gases, 3) abate these gases at considerable financial and environmental cost, 4) capture and recycle of PFC's from the exhaust lines.

Air Liquide America has recently developed a patented membrane-based PFC recycle system which can capture more than 95% of these gases from the process exhausts. Among the PFC's, the capture efficiency for SF₆, CF₄ and C₂F₆ exceeds 98%, and at the same time, the system can concentrate these gases from a few ppm to more than 99%. This paper will review the options for the emission reduction, and discuss in detail the technology aspect of the Air Liquide's recycle system.

INTRODUCTION

The greenhouse effect is a natural phenomenon, it keeps the earth warm enough to habitats. It relies upon the presence of global warming gases in the atmosphere that traps heat and warm the planet surface. Since the

industrial revolution, human activity has been increasing global warming gas concentrations. As a consequence of building-up these heat trapping gases, it is expected to change the regional and local climate conditions including temperature, precipitation, and sea level.

Global warming gases are chemicals that are capable of trapping solar radiation in the earth's atmosphere. They include both naturally occurring gases like carbon dioxide, methane, etc, and human-made compounds like PFC's. These gases are ranked by its global warming potential (GWP) which is related with their estimated atmospheric lifetimes and radiation absorption constant relative to the most abundant greenhouse gas, carbon dioxide. The concept of GWP allows one to compare the ability of each global warming gas to trap heat in the atmosphere. Table 1 summarizes the global warming potentials of some of the PFC's. Of all the greenhouse gases, PFC's including CF_4 , C_2F_6 and SF_6 are identified as the most potent global warming gases due to their stability in atmospheric conditions and strong radiation absorption. For example, SF_6 is about 23,900 times more potent than CO_2 .

Environmental scientists believe that the buildup of these greenhouse gases in atmosphere will drastically alter the climate: causing more severe storms, droughts, floods, and melt more polar ice, thus raising sea levels with disastrous results. All of the global warming gases emitted will exist in the atmosphere for several hundreds of human generations, so actions must be taken to address the emission reduction.

United States is actively pursuing a course to limit the emission of these very potent global warming gases. In 1997 Kyoto Protocol, the U.S., the Europe Union, and Japan are committed to reduce the global warming gases emissions by 7%, 8% and 6%, respectively, based upon 1990 emission levels.

Semiconductor manufacturers use large quantities of PFC's for etching and reactor cleaning processes. These processes, however, are inefficient and as much as 70% of the PFCs are not converted to reaction products and leave the process. Since early 1994, this industry has been proactively researching on various options addressing the emission reduction of these global warming gases from the manufacturing processes. Air Liquide, as an industrial gas supplier, has been very actively working with this industry to develop various technologies, addressing the need of the industry and the environment.

EMISSION REDUCTION OPTIONS FOR SEMICONDUCTOR INDUSTRY

The semiconductor industry has been working on several emission reduction options. These options can be classified into four groups: 1) change of process chemistry so that it eliminates the usage of PFC's; 2) optimizing the process efficiency so that it emits less PFC's to the environment; 3) capture and recycle of these emitted PFC's, and 4) abate the PFC's from the process exhaust lines. Table 2 summaries the strength and weakness of each different emission reduction technologies.

MEMBRANE-BASED PFC RECYCLE TECHNOLOGY

Generally, the recycle process is composed of two stages: a pretreatment stage for the removal/naturalizing hazardous species in the process exhaust, and a recovery stage to separate and concentrate PFC gases from air gas. Depending upon specific situations, the recovered PFC's can either be reused directly on-site or sent to PFC's manufacturers as a feed-stock (Figure 1). The selection of pretreatment technology is process exhaust dependent, while the recovery stage is more generic.

The primary function of the Air Liquide system is to recover the PFC's, which are heavily diluted in nitrogen, from the semiconductor manufacturer's process exhaust lines. The recovery is done by concentrating these gases from parts per million (ppm) level to greater than 95%. The recovered and concentrated PFCs may be either directly used for low purity applications or further purified before being reused for high purity applications at the semiconductor manufacturing facility.

The recovery process is based upon a separation technology with glassy asymmetric composite hollow fiber membranes developed and manufactured in-house. This membrane takes advantage of the molecular size difference between the PFC's and air gases. The air gases permeate through the membrane, enriching the concentration of PFC's. Since PFC's have a low permeability through this membrane, there are few losses of

Table 1. Global warming potentials (GWP)

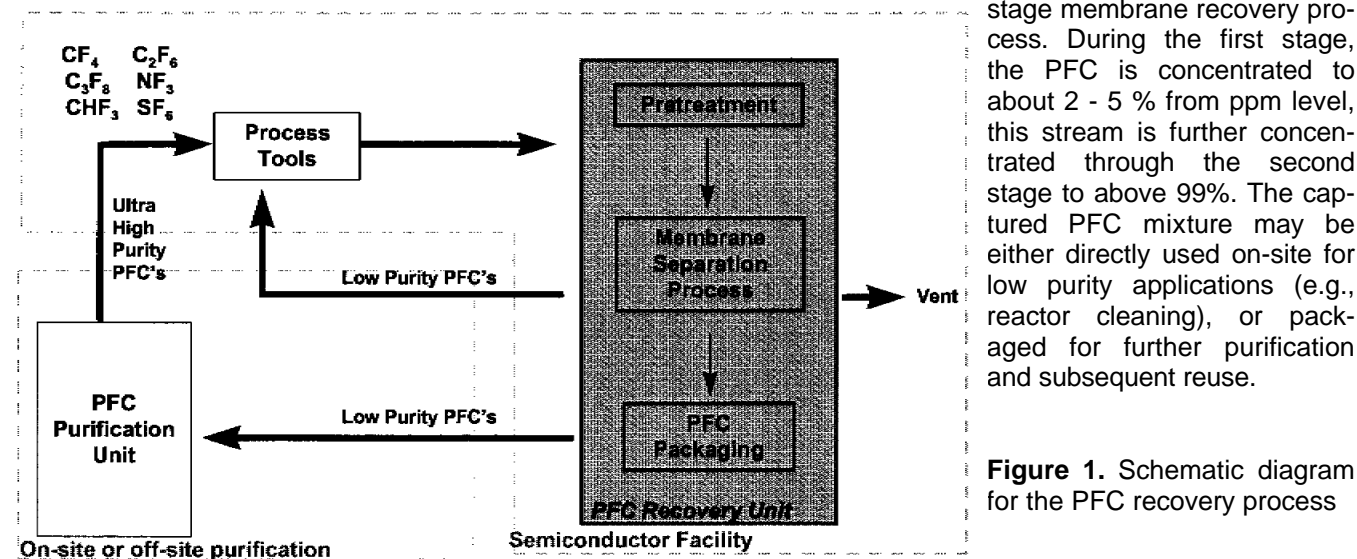
GAS	Lifetime (year)	GWP ₁₀₀
SF_6	3,200	23,900
NF_3	740	13,100
CHF_3	250	11,700
C_2F_6	10,000	9,200
C_3F_8	2,400	7,000
CF_4	50,000	6,500
CO_2	200	1

PFCs in the vented air gas stream. More than 95% of the PFC's remains in the stream and is recovered.

Table 2. Comparison of different PFC emission reduction technologies

Technology	Strength	Weakness
Combustion based abatement	<ul style="list-style-type: none"> Commercially available Currently in use 	<ul style="list-style-type: none"> By-product management (e.g., HF, etc.) High cost/safety issues for hardware & consumable (fuel) Limited efficiency for CF₄ destruction
Plasma based abatement	<ul style="list-style-type: none"> Incorporated on pure process stream Commercially available No external chemical/fuel 	<ul style="list-style-type: none"> By-product management (e.g., HF, etc.) Gas back-diffusion to process tool Limited efficiency for CF₄ destruction
Chemical-Thermal based abatement	<ul style="list-style-type: none"> No external chemicals/fuel Commercially available 	<ul style="list-style-type: none"> By-product management (spent solid disposal) Plugging, breakthrough of packed bed Limited efficiency for CF₄ Qualification at manufacturing site
Process optimization	<ul style="list-style-type: none"> Less expensive than abatement No feedstock changes to process 	<ul style="list-style-type: none"> PFC emission still present bw at lesser degree Not a long term viable solution Qualification at manufacturing site
Alternative process chemistry	<ul style="list-style-type: none"> Lower emissions with new precursors 	<ul style="list-style-type: none"> PFC emissions still present in some cases Not commercially available New process qualification at manufacturing site
Capture & recycle	<ul style="list-style-type: none"> No external chemicals/fuel No hazardous chemicals generation Value for the recovered products 	<ul style="list-style-type: none"> Operating cost for the total management system for situations where PFC emissions are still allowed

Prior to entering the membrane process, the exhaust gases are first treated to remove hazardous compounds (such as HF, COF₂, SOF₂, WF₆, etc.) in a scrubber system. The stream is then compressed and sent to a two



This PFC recovery system has been tested extensively in two separate semiconductor manufacturers, and went through a rigorous qualification test under the umbrella of SEMATECH, a research consortium for semiconductor

manufacturers. The test results demonstrated that the membrane-based system offers PFC capture efficiency in excess of 95% with the captured PFC concentration above 99%. This technology has shown stable performance under widely variable feed conditions.

The advantages of the membrane system are that it does not need a drying process, the moisture in the exhaust line will permeate with air through the membranes; it can handle a large range of flowrate, from a few standard liters per minute to above thousand liters per minute due to its modular nature; it is very compact, therefore, it can be placed in areas where space is very expensive, e.g., semiconductor chip manufacturers; and it does have moving parts in the system, which reduces the operational cost.

SUMMARY

Although uncertainty exists about exactly how earth's climate responds to these gases, the global temperatures are rising. All of the global warming gases emitted will exist in the atmosphere for several human generations, so actions must be taken to address the emission reduction. Though there is no magic bullet for complete reduction, there are several options for the emission reduction of most potent global warming gases, namely, PFC's: process chemistry alteration, process improvement, recycling and abatement.

The process chemistry alteration is a long term option, it can not address the immediate goal of emission reduction. The abatement technology is commercially matured one, but it does not address the roots of the pollution problem. It transforms from a global warming issue into a hazardous waste management problem, and is expensive to operate due to its requirement of external energy in the forms of fuel and/or electricity. Both the process improvement in order to increase the raw PFC's material utilization rate and the PFC recycle options, not only benefit the industry itself economically, but also the society by decreasing the PFC emission.

The membrane-based PFC capture/recycle system is well suited for capture highly diluted PFCs in the exhaust lines due to its extremely high separation factors. Among the PFC's, the capture efficiency for SF₆, CF₄ and C₂F₆ exceeds 98%, and at the same time, the system can concentrate these gases from a few ppm to more than 99%.

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SEPARATION OF DILUTE ACETIC ACID FROM WATER BY PERVAPORATION USING AMINE-FUNCTIONAL PDMS MEMBRANES

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Organic solvents for the extraction of dilute acetic acid from water often include a Lewis base such as triethylamine or trioctylphosphine oxide to improve the separation factor through chemical complexation. However, both the Lewis base and the organic solvent can be soluble in the aqueous phase, thereby generating

a potential wastewater stream. Pervaporation, an emerging membrane separation process for systems difficult to separate by distillation, could be utilized as a means of pollution prevention in these applications by reducing energy demand and eliminate the need for a third component. In this paper, the concept of chemical complexation is extended to the incorporation of covalently bound tertiary amine groups in the backbone of polydimethylsiloxane (PDMS) membranes. This work focuses on the removal of acetic acid from dilute aqueous solutions and tests the applicability of pervaporation for this separation. Experiments were performed with modified and unmodified PDMS membranes in order to quantify the differences when incorporating complexation.

To better understand the complex transport mechanisms operative in membranes containing Lewis-base groups, FTIR-ATR (Fourier-Transform Infrared, Attenuated Total Reflectance) spectroscopy was used to characterize acetic acid and water in PDMS films containing tertiary amine groups. These results were used in conjunction with the pervaporation results in order to further elucidate the diffusion mechanism. The infrared spectra indicate three forms of acetic acid are present: single molecules, dimers and carboxylate ions. The last form provides evidence of chemical complexation between the acetic acid and tertiary amine and is absent in the spectra for unmodified PDMS membranes.

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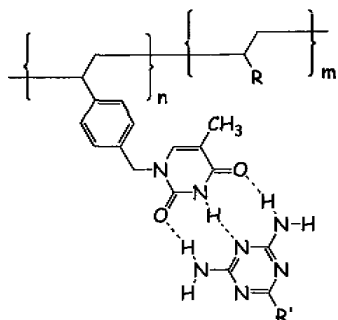
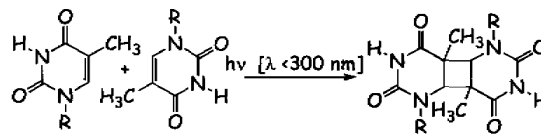
MATERIALS

HYDROGEN BOND MEDIATED PHOTO-DIMERIZATION IN SYNTHETIC ANALOGS OF DNA: ENVIRONMENTALLY BENIGN PHOTORESISTS

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Thymine, one of the four nucleotide base constituents of DNA, photodimerizes at wavelengths $< 300\text{nm}$. As pendant substituents of polymeric nucleic acid chains, this photocyclization reaction has been identified as a significant physiological event in both the cause and treatment of several afflictions. Synthetic polymers incorporating thymine have been investigated in order to exploit this process. Environmentally benign, water soluble photoresists have been prepared. Highly efficient photosensitivity is observed.



Thymine and derivatives also participate in triple hydrogen bonding. It is possible to non-covalently link functional molecules to these polymeric thymines.

This presentation will discuss the effect of hydrogen bonding on the photochemistry of polymeric thymines and environmentally benign applications of these systems will be illustrated.

POLY(ASPARTIC ACID): A POLYMER DESIGNED TO BIODEGRADE IN A DISPOSAL SITE OF CHOICE

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Many polymers are discarded into the environment after use. This is both deliberate disposal and careless littering. The latter a social problem and can be addressed by laws. The former represents a challenge to polymer manufacturers to develop new polymers that will biodegrade in the disposal sites that they enter and, therefore, not be able to enter the environment for possible negative impact. We have addressed water-soluble polymers since these are a major potential problem in the environment, though no adverse effects have been noted to date for most of these polymers, and all testing indicates this is unlikely. However, even with a low probability for there to be an environmental impact, we feel it wiser to evaluate the possibility of developing biodegradable alternatives to polymers such as poly(acrylic acid).

Poly(aspartic acid) is a water-soluble polymer designed to replace poly(acrylic acid)s, the largest volume water-soluble polymers in the commercial world. They are obtained from petroleum feed-stocks through oxidation to and polymerization of acrylic acid. These polymers are used widely in applications such as detergents, mineral dispersants, water-treatment, super-absorbents etc. Many issues have been raised on their non-biodegradability and ultimate fate in the environment, particularly super-absorbents in diapers disposed in landfill and detergents in wastewater treatment plants. Thus, the goal of the work was to develop suitable alternatives that would be biodegradable in the appropriate disposal site.

Before synthesizing biodegradable polymers, a test methodology is needed to establish when a polymer will meet the goal of the program. In the case of water-soluble polymers which are targeted here, disposal is anticipated to be in wastewater treatment facilities for detergents and in a compost facility for super-absorbents. Suitable tests should be able to establish that complete biodegradation has occurred in the residence time of the disposal site. For wastewater treatment, this is a few hours to a few days depending on whether the polymer is completely soluble in the aqueous media or is deposited on the solid mass, respectively. For compost, a few weeks should be sufficient for complete biodegradation. Standard tests are available in both cases.

Poly(aspartic acid) salts may be synthesized from L-aspartic acid by thermal condensation to yield polysuccinimide which is then readily hydrolyzed with base. This condensation may be done in the presence or absence of an acid catalyst. In the absence of catalyst, molecular weight is limited to about 5000 Daltons, in the presence of catalyst molecular weight may be controlled in the range of 5000 to 100,000. An alternative synthesis utilizes the thermal condensation of maleamic acid which gives a polymer very similar to that obtained from L-aspartic acid in the absence of catalyst. Only the acid catalyzed condensation of L-aspartic acid yields a product that meets the technical and biodegradation requirements. This polymer has a linear structure and rapidly biodegrades in a sewage treatment inoculum indicating its acceptability as a detergent polymer to replace poly(acrylic acid).

Using the acid catalysis process, high molecular weight polymers were developed as precursors for super-absorbent polymers. These linear high molecular weight polymers may be crosslinked to produce polymers equivalent to commercially available poly(acrylic acid) superabsorbent. These products are degradable with enzymes in laboratory testing and likely to be biodegradable in compost facilities.

We have clearly demonstrated that poly(aspartic acid)s are prime technical candidates for replacing poly(acrylic acid)s in many applications where biodegradability is an issue. The major issue to be overcome is the cost barrier where poly(acrylic acid)s have a clear advantage. This and the lack of any obvious harmful environmental effects are the reasons poly(acrylic acid) will remain the polymer of choice in the foreseeable future in detergents and superabsorbent polymers.

WATER-BORNE OIL-MODIFIED POLYURETHANE COATINGS VIA HYBRID MINIEMULSION POLYMERIZATION

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INTRODUCTION

Oil-modified polyurethanes (OMPU) are, in terms of volume produced and sold, the most important polyurethane coatings, with superior properties such as gloss, chemical resistance and film formation. Most urethane coatings are solvent-based, and solventbased coatings are less than desirable due to the environmental impact of their high volatile organic compounds (VOC). To meet the increasing concern for health, safety and the environment, there has been a strong preference in recent years for water-borne coatings. Wang et al.¹ have demonstrated the production of acrylic/alkyd graft copolymers for coatings applications by hybrid miniemulsion polymerization. The object of this work was to obtain oil-modified polyurethane grafted onto polyacrylics by free radical polymerizing acrylic monomers in the presence of oil-modified polyurethane resin via hybrid miniemulsion polymerization.

In miniemulsion polymerization, an effective surfactant/hydrophobe system is used to stabilize very small monomer droplets (50 - 500nm). In order to break up monomer droplets to such size, high agitation is applied by sonication or homogenization.² The hydrophobe is a highly monomer-soluble, highly water-insoluble material added to increase diffusional stability of the emulsion. The large droplet surface area in miniemulsion (because of small droplet size) results in most of the surfactant being adsorbed to the droplets with little free surfactant available to form micelles or stabilize aqueous phase polymerization. Therefore the predominant nucleation mechanism in miniemulsion polymerization is droplet nucleation. In contrast, in miniemulsion polymerization, polymerization takes place in the (very small) droplets, in the presence of the polyurethane resin, and without the need for diffusion of the resin across the aqueous phase. If a conventional emulsion polymerization were run in the presence of the OMPU, the result would be polyacrylic particles in a physical blend with dispersed polyurethane, with very little chance of grafting between the two species

EXPERIMENTAL

Emulsion Preparation and Polymerization

Miniemulsion were prepared and polymerized according to the recipes shown in Table 1. The desired amount of

sodium lauryl sulfate (SLS) was dissolved in about 220 g of DI water and potassium persulfate (KPS) was dissolved in about 30 g DI water. Benzoyl peroxide (BPO) was dissolved in the acrylic monomer mix, and the OMPU was added. Oil-modified polyurethane 138-0634 supplied by McWhorter Technologies was used. The mixture was stirred for several hours to complete dissolution of the OMPU. Then the oil phase was added to the SLS solution and sheared for 5 minute at high speed with a magnetic stirrer. This pre-emulsion was then sonicated for 15 minutes at 70% output with the Fisher 300W Sonic Dismembrator. Polymerization was carried out at 80 °C. Monomer conversion was determined gravitometrically.

RESULTS AND DISCUSSION

Polymerization

Miniemulsions prepared using only the OMPU as hydrophobe were stable for up to five months, indicating diffusional as well as colloidal stability. Both the droplet and polymerized particle diameters were in the 100-300 nm range. Particle size changed only slightly over the course of the polymerization, indicating preponderant droplet nucleation.

Polymerizations were carried out according to the recipes in Table 1. The rates of polymerization decreased with increasing OMPU. This suggests that the resin might be retarding the polymerization. Linseed oil-modified polyurethane was used as the resin. The main fatty acids in linseed oil are linolenic, linoleic, oleic, and less than 10% saturated fatty acids. During polymerization, grafting can occur by chain transfer from the propagating free radical to the resin. The resulting fatty acid radical may be substantially less reactive than the acrylic radical, resulting in a reduction in polymerization rate. Alternatively, grafting may occur by copolymerization between the polymerizing radical and the double bonds of oil-modified polyurethane, resulting again in a less active radical. Either mechanism would give graft copolymer, and either might result in retardation or the rate of polymerization.

Product Characterization

The determination of grafting efficiency will determine if grafting has occurred, or if the product is a blend of polyacrylic homopolymer and polyurethane. Curing ("drying") in oil-modified polyurethane occurs through reactions of the residual double bonds in the fatty acids with atmospheric oxygen in much the same way as in the alkyd resins in common oil-based paints. Because the drying reactions require residual double bonds, it is important to know what fraction of the original double bonds in the fatty acids have been reacted during the polymerization process. Since many of the fatty acids have more than one carbon-carbon double bond, it is possible to have crosslinked material. Polymer which is heavily crosslinked will not form good films, and so it is important to determine the percentage of crosslinked material.

¹³C NMR was used to determine the residual double bond concentration. The carbon in the urethane bond was used as internal standard because its concentration will not change during polymerization. Results indicate that 60 to 70 % of the original fatty acid double bonds remain after polymerization. This should give adequate sites for drying.

The crosslinked percentage is defined as the weight percent of the total polymer that is crosslinked. To determine the crosslinked percentage, chloroform, toluene, THF and 1,4-dioxane were used sequentially to extract soluble polymer. The remaining polymers after all extractions were assumed to be crosslinked: For all samples, crosslinked percentage was less than 4.8%. At this level, it should not adversely affect the film forming properties of the latexes.

The grafting efficiency is defined as the percent of the total acrylic monomer polymerized which is grafted to the OMPU. Ethyl ether is a good solvent for OMPU, but does not dissolve polyacrylics at all. Thus, it was used to determine the grafting efficiency of polyacrylics: Grafting will enhance the miscibility between polyacrylics and the resin, which in turn will benefit the film in properties formed by the latex. All of the latexes had a grafting efficiency of at least 29%.

GPC measurements were used to determine the molecular weight of the products. The chromatograms for each sample showed three significant peaks. The number average molecular weight was calculated for each peak separately. The area of the highest MW peak increased with the increasing ratio of acrylic to resin. The molecular weight of this peak is in the range of several tens of thousands and is probably pure polyacrylic or graft polymer. The molecular weight of the next peak was approximately 4,500 which corresponds to that of OMPU. As expected, the peak area increased as the acrylic-to-resin ratio decreased. The last peak had a molecular weight of approximately 1,500 - 2,000 which is substantially lower than that of resin, and its area increases with

the increasing ratio of monomer to resin. These two factors indicate the possibility of low molecular weight acrylic oligomers generated by the chain transfer.

Morphology and Coating Properties

Dynamic mechanical analysis was used to look for evidence of graft copolymer and homopolymer. Each sample had the same glass transition at 35 °C that corresponds to the T_g of pure polyacrylics. Although the glass transition of other components does not appear on the DMA spectrum at the recording temperature range, this result indicates that polyacrylic was phase-separated from other possible components in the films. TEM analysis to confirm this was not conclusive since no evidence of heterogeneity was evident in the latex particles. Only the osmium tetroxide-stained phase (OMPU) could be seen, suggesting a core/shell structure with a resin-rich shell.

Film hardness and film adhesion was measured on films cast from latex. The films were dried at room temperature for two days. Adhesion was good for all samples. Hardness for all samples was "B". Addition of commercial drying agents increased the hardness to "HB". After three months all the samples reach "H1".

CONCLUSION

Based on the study presented here and previous research,¹ the hybrid miniemulsion polymerization process has been shown to be a promising technology for converting solvent-based coatings into environmentally-friendly water-based coatings. By employing resin as both reactant and hydrophobe, higher purity of product can be achieved, since no additional hydrophobe is required. Films obtained from the acrylic/OMPU latexes show good adhesion property and fair hardness property. Mixed metal drying agents can enhance the drying rate substantially.

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Table 1. Recipe for Miniemulsion Polymerization

Miniemulsion	Ingredients (wt)				
	OMPU	MMA	BA	AA	BPO
1	100	49	50	1.0	0.5
2	60	49	50	1.0	0.5
3	30	49	50	1.0	0.5
4 ^a	0	49	50	1.0	0

The continuous phase consisted of 200 parts water/100 parts total solids, 0.02mol KPS/L water and 0.02mol SLS/L water; BPO: 0.5 wt% (based on monomer)

MMA = methyl methacrylate; BA = butyl acrylate; AA = acrylic acid

^aRun 4 was run to obtain pure polyacrylics where 2 g PMMA was employed as hydrophobe, and the reaction temperature was 60°C

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CATALYTIC SYNTHESIS

SUPERCRITICAL 1-BUTENE/ISOBUTANE ALKYLATION ON SOLIDACID CATALYSTS FACILITATED BY CARBON DIOXIDE¹

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Alkylation reactions are used industrially to convert light refinery gases (C₃-C₅) into gasoline range compounds (C₇-C₉). At present, alkylates constitute roughly 13% of the U.S. gasoline pool and play an important role in meeting the reduced emissions gasoline requirements established by the 1990 Clean Air Act. Industrial alkylation processes employ either hydrofluoric acid or sulfuric acid as catalyst. The cost of acid regeneration as well as the environmental hazards resulting from transportation and disposal of the acid sludge underscore the need for a more economical and environmentally-friendlier alkylation technology. The use of solid acids as an environmentally-safer alternative to hydrofluoric or sulfuric acids has long been recognized. As reviewed elsewhere (Corma and Martinez, 1993; Rao and Vatcha, 1996), numerous efforts aimed at developing solid acid alkylation catalysts and solid acid-based isobutane-olefin alkylation processes have been reported for more than three decades. However, to-date, none of the solid alkylation catalysts has gained acceptance in industry primarily due to rapid catalyst deactivation due to coke formation. In gas-phase media, the heavy coke precursors (such as olefinic oligomers) are poorly soluble while in liquid phase, reaction media, the transport of coke precursors out of the catalyst pores is severely restricted resulting in their readsorption and transformation to consolidated coke.

"Supercritical" alkylation, performed with excess isobutane ($P_c = 36.5$ bars; $T_c = 135^\circ\text{C}$) above the critical temperature (T_c) and critical pressure (P_c) of isobutane, has been reported to slow down deactivation of solid acid catalysts (Hussain, 1994; Fan et al., 1997). The liquid-like densities and enhanced transport properties of supercritical fluids are exploited to extract coke precursors *in situ*, and thereby, to obtain extended catalyst activity. However, at reaction temperatures exceeding 135°C , undesirable side reactions such as oligomerization and cracking occur, resulting in unacceptable product quality. Although lower temperatures enhance C₈ alkylate selectivity, rapid catalyst deactivation due to coke formation is a problem on solid acid catalyst even at temperatures as low as 50°C .

To lower the critical temperature of the alkylation reaction mixture, we employ carbon dioxide ($P_c = 71.8$ bars; $T_c = 31.1^\circ\text{C}$) as a low T_c diluent. This allows supercritical operation at reaction temperatures below the critical temperatures of the reactants (135°C for isobutane and 140°C for 1-butene) while exploiting the liquid-like densities and gas-like transport properties of supercritical fluids. The lower reaction temperatures favor alkylation reactions over oligomerization and therefore reduce catalyst deactivation. The liquid-like densities of the supercritical reaction favor oligomer (i.e., coke precursor) solubilization, while the gas-like diffusivities and viscosities enhance the removal of butene, oligomers from the catalyst before they undergo further consolidation and deactivate the catalyst. Details of the experimental unit are provided elsewhere (Clark and Subramaniam, 1998).

Table 1. Experimental Conditions

Temperature (°C)	Pressure (bars)	Feed CO ₂ :I:O ¹ (molar)	Reaction Mixture Phase
140	34.5	0:9:1	gas
50	34.5	0:9:1	liquid
140	60.7	0:9:1	near-critical
50	155.1	86:8:1	supercritical
95	137.9	43:8:1	supercritical

Olefin Weight Hourly Space Velocity = 0.25 kg/kgcat/h

¹I = Isobutane; O = Olefin (1-butene)

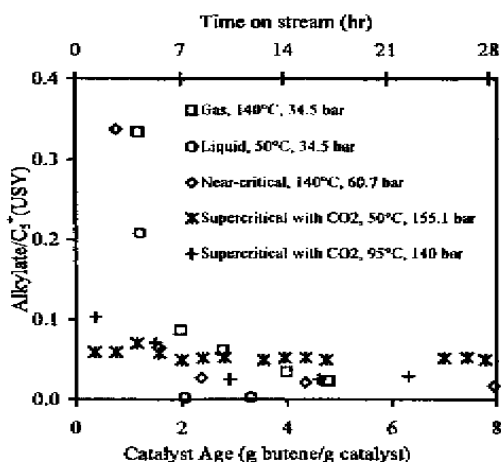


Figure 1. Alkylate production rate histories on a USY catalyst in various reaction phases (Experimental conditions are listed in Table 1).

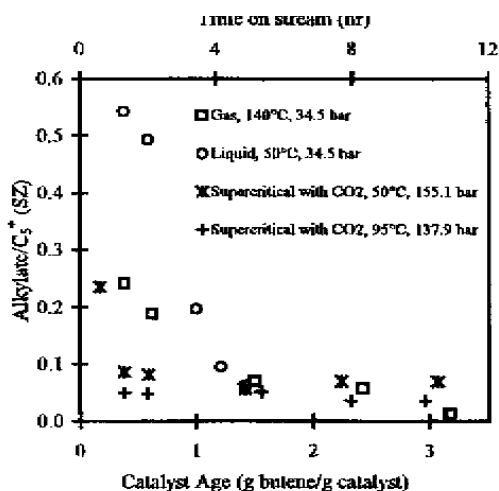


Figure 3. Alkylate production rate histories on a SZ catalyst in various reaction phases (Experimental conditions are listed in Table 1).

Figure 1 compares the alkylate fraction of the C_{5+} products versus catalyst age in reaction phases ranging from gas-like to liquid-like physical properties in the bulk fluid phase. At 140°C and 34.2 bars, which is above the critical temperature of isobutane but below the critical pressure of isobutane, the bulk-phase reaction mixture is subcritical and is termed "gas-phase" reaction mixture. At 140°C and 60.3 bars, which is above the critical values for isobutane, the reaction mixture has been termed "supercritical" by both Hussain (1994) as well by Fan et al. (1997). Liquid reaction mixture can be realized in the bulk phase when the reaction temperature is less than the critical temperature of isobutane and the pressure is sufficiently high. Accordingly, the run at 50°C and 35 bars is termed the "liquid-phase" run. The alkylate production declines continuously with time in all these runs, the steepest decline occurring at supercritical conditions. It follows from both our results and those of Fan et al. that supercritical operation without carbon dioxide does not produce stable alkylate production in the time frame studied. *In sharp contrast, the alkylate production attains a nearly steady value after a few hours on stream during the supercritical runs employing carbon dioxide.* Even though the alkylate fraction in the product is small (around 5%), the steady alkylate production is an indication that supercritical operation employing carbon dioxide as a diluent is capable of maintaining the activity of the strong acid sites at a constant level for the duration of the experiments (nearly 30 hours). In other words, the supercritical reaction medium solubilizes and removes the coke precursors from the strongest acid sites preventing the transformation of coke precursors into consolidated coke. *Extended runs for up to nearly two days on the H-USY catalyst continued to show stable alkylate production activity.*

Table 2. Comparison of Fresh and Spent USY Catalyst Characteristics

Reaction Phase	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Observed Color
Fresh	560	0.33	white
Liquid Phase	350	0.22	beige
Gas Phase	130	0.09	brown
Near-critical	190	0.13	brown
Supercritical	430	0.25	off-white
Supercritical	420	0.25	beige

I = Isobutane

O = Olefin (1-butene)

The ability of the carbon dioxide-based supercritical reaction mixtures to mitigate coking and thereby to maintain better pore accessibilities is also evident from the narrow product spectrum (confined to C_8 's), the lighter color of the spent catalyst samples, and relatively low surface-area and pore-volume losses (< 25%) in the spent catalysts (Table 2). Similar results will be presented for other solid acid catalysts such as sulfated zirconia (Figure 2), zeolite beta and Nafion. The carbon dioxide-based, fixed-bed, supercritical process thus eliminates a major technological barrier impeding the application of solid acid catalysts in alkylation practice and shows promise as an environmentally-safer alternative to conventional alkylation that employs liquid acids.

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**Extended abstract not received in time for printing.
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FLUOROUS BIPHASIC CATALYSIS. SYNTHESIS OF A TRIS-N-[C₈F₁₇(CH₂)₃]₃-1,4,7-TRIAZACYCLONONANE LIGAND AND COMPLEXATION WITH [Mn(C₈F₁₇(CH₂)₂CO₂)₂] AND ITS Co²⁺ ANALOG TO PROVIDE PERFLUOROHEPTANE SOLUBLE PRECATALYSTS FOR ALKANE AND ALKENE FUNCTIONALIZATION

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Fluorous biphasic catalysis (FBC) is a new concept for homogeneous catalysis where the fluorocarbon soluble catalyst and the substrates/products reside in separate phases. We present the synthesis of a new fluoro ponytailed ligand, tris-N-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl)-1,4,7-triazacyclononane (R_fTACN) that is soluble in perfluoroalkanes, and new, monomeric Mn²⁺ and Co²⁺ fluoro ponytailed carboxylate synthons, [Mn(O₂C(CH₂)₂C₈F₁₇)₂] and [Co(O₂C(CH₂)₂C₈F₁₇)₂]. The initial results on the functionalization of alkanes / alkenes, using *in situ* generated, fluorous phase soluble R_fMn²⁺-R_fTACN and R_fCo²⁺-R_fTACN complexes as the catalysts, in the presence of TBHP and O₂ gas, will be discussed. These FBC studies were funded by Elf Aquitaine Inc and DOE.

ENVIRONMENTALLY BENIGN CO INSERTION ON SUPPORTED METAL CATALYSTS

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ABSTRACT

Isocyanate synthesis from the reaction of CO with nitrobenzene has been studied on supported Pd, Rh and Ce-promoted catalysts. Infrared observation of the acyl species generated during the reaction of nitrobenzene with adsorbed CO indicates the occurrence of the CO insertion into the adsorbed nitrene on the surface of supported metal catalyst. Results of the studies demonstrate that carbonylation on supported metal catalysts may provide an environmental benign route for isocyanate synthesis in a solvent free environment and may allow the simultaneous separation of products and catalyst.

INTRODUCTION

The CO insertion reaction is considered by the chemical industry as the most promising, environmentally benign synthesis pathway for replacing the highly hazardous conventional method of isocyanate synthesis from the phosgene-amine reaction¹. It has been suggested that the CO insertion pathway to isocyanate may involve the following steps: (i) the formation of nitrene from the interaction of nitrocompound with the metal catalyst, (ii) the insertion of CO into the metal-N bond of the adsorbed nitrene, (iii) the formation of isocyanate and regeneration of the catalyst. Both metal complexes and oxide-supported metals have been used as catalyst precursors for the

carbonylation reaction in solvents. There are doubts whether the reaction does take place on the surface of the supported metal catalysts. It has been speculated that the metal component on the catalyst surface dissolves in the solvent forming the active complex, which catalyzes the reaction. Oxide supported metals may provide distinct advantages over metal complexes because of the ease of separation of solid catalysts from the reactant and product mixture. However, lack of mechanistic understanding of the reaction has greatly hindered the development of an efficient industrial process.

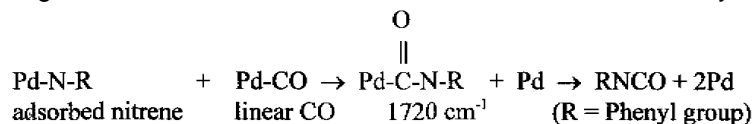
The objectives of this paper were to develop a fundamental understanding of the isocyanate/carbamate synthesis mechanism on the surface of supported Rh and Pd catalyst, and to utilize the mechanistic and material synthesis chemistry information obtained to tailor the surface sites for maximizing the catalyst activity. *In situ* infrared (IR) coupled with a transient approach was employed to determine the reactivity of adsorbed CO, to identify the active adsorbates and the rate limiting step, and to investigate the promotional role of surface Lewis acid in CO insertion.

RESULTS AND DISCUSSION

Carbonylation of nitrobenzene/aniline with ethanol was carried out on the Rh/Al₂O₃, Pd/Al₂O₃, and Cerium-promoted Rh and Pd catalysts. The reactions are as shown below.

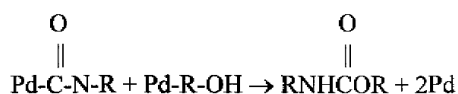
- I. $\text{RNO}_2 + 3\text{CO} \rightarrow \text{RNCO} + 2\text{CO}_2$
 - II. $\text{RNH}_2 + \text{CO} + \text{H}_2 \rightarrow \text{RNCO} + \text{H}_2\text{O}$
 - III. $\text{RNO}_2 + 3\text{CO} + \text{R}'\text{OH} \rightarrow \text{RNHCOOR}' + 2\text{CO}_2 \rightleftharpoons \text{Carbamate Synthesis}$
- R is either alkyl or phenyl group.

Fig 1 (a) shows the exposure of the reduced Ce-Pd catalyst to gaseous CO at 313 K produced a linear CO band at 2071 cm⁻¹ and bridged CO band at 1905 cm⁻¹. Exposure of adsorbed CO to nitrobenzene (C₆H₅NO₂) at 313 K led to the disappearance of linear CO and growth of a broad band around 1720 cm⁻¹, which was further verified as the acyl group suggesting occurrence of the insertion of linear CO in adsorbed aryl nitrene as shown in Fig. 1



(b).

The insertion of CO into adsorbed aryl nitrene appears to resemble the CO insertion into adsorbed alkyl in heterogeneous hydroformylation³. Further exposure of the catalyst and adsorbates to ethanol at 313 K led to the observation of carbamate species shown in Fig. 1 (c), indicating that carbamate synthesis can take place on the catalyst surface.



The objective of the above step, addition of ethanol, is to convert the isocyanate to carbamate species, i.e. N-phenyl ethyl urethane, because of the toxic nature of the isocyanate species. N-phenyl ethyl urethane is an important industrial intermediate².

The absence of IR-observable Pd carbonyl and the involvement of adsorbed CO in the formation of adsorbed acyl and carbamate species provide strong support for the occurrence of carbonylation of nitrocompounds on the surface of Ce-Pd catalysts. This paper, for the first time, reports unambiguous identification of carbonylation on metal surfaces. The Rh and Pd surface states have been compared with respect to the reactivity of adsorbed CO for insertion into the metal nitrene bond and the overall catalyst activity and selectivity. The proposed reaction mechanism and its implication for the development of a heterogeneous catalyst system for isocyanate/carbamate formation is elaborated.

SUMMARY

Carbonylation of nitrobenzene and aniline was studied over Rh/Al₂O₃, Pd/Al₂O₃, and Cerium-promoted Rh and Pd catalysts using *in situ* Infrared (IR) technique at 313-523 K and 0.1-1.7 MPa. Linear CO on Pd and Rh surfaces was found to be involved in the insertion reaction with adsorbed aryl nitrene, leading to the formation of the isocyanate species. Subsequent addition of alcohol resulted in conversion to the stable carbamate species. Results of the studies demonstrate carbonylation on supported metal catalysts may provide an environmental

benign route for isocyanate synthesis in a solvent free environment and allow the simultaneous separation of products and catalyst.

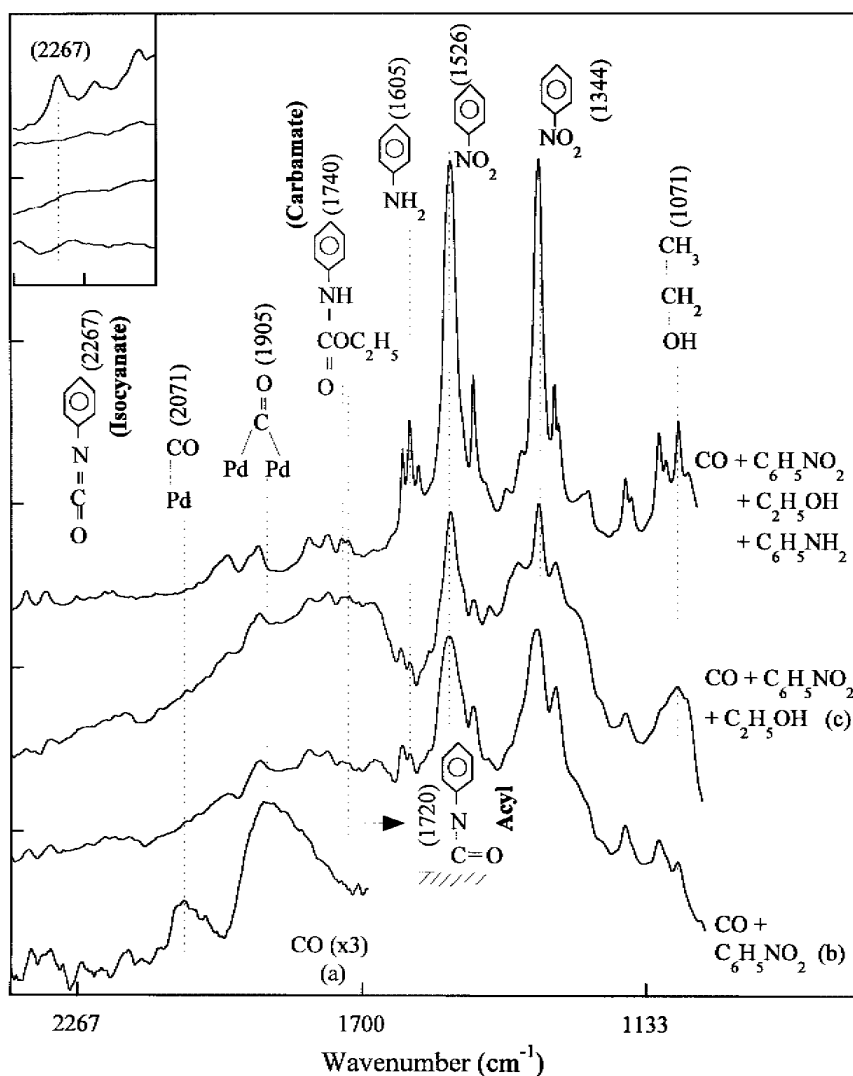
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Fig. 1. Carbonylation of Nitrobenzene on Ce-Pd/Al₂O₃ at 313 K



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SOLVENTLESS

SOLVENTLESS COATING FORMULATIONS FOR MAGNETIC TAPE MANUFACTURE

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ABSTRACT

Significant progress was made toward identifying a binder materials package that would enable a solventless magnetic tape manufacturing process that would eliminate the possibility of air pollution. Mixtures of commercial acrylate monomers and acrylate-terminated urethane oligomers gave electron beam cured films with good tensile properties and adequate adhesion to the polyester base film. The binder polymers suffered no significant decrease in tensile strength after accelerated aging. Commercial magnetic particles were treated with a methacrylate-functionalized silane coupling agent, which enabled the preparation of dispersions with rheological properties that approach those of conventional solvent-based formulations. A preliminary comparison of the economic of the solventless process with a conventional solvent-based process, showed the solventless process to be slightly lower in cost.

INTRODUCTION

Magnetic tape consists of a magnetic coating on a polyester base. The coating contains magnetic particles held to the base with a polymeric binder and other additives, such as lubricants, carbon black and alumina. Tape is manufactured using a continuous web coating process that uses organic solvents, such as MEK, MIBK, toluene, and THF. MEK, MIBK and toluene are on the EPA's list of hazardous air pollutants. We have estimated that a modern tape coating line uses 600 kg of organic solvents per hour.¹ The industry meets air emissions regulations by using solvent capture, recovery and recycle systems. Industry sources tell us that 93 to 95% of the solvents are recovered, meaning 5 to 7% escape to the environment. Assuming the coating lines 4000 hr/yr (two eight hour shifts per day, five days per week, 50 weeks per year), then the potential emission would be 120 to 17 metric tons per coating line per year. The objective of our research project is to reduce the air emissions to zero.

Our approach is to replace the organic solvents with a mixture of liquid acrylate monomers. The monomers would serve as the solvent for the coating fluid. After coating and electron beam irradiation, the monomers would undergo free radical polymerization to form the binder. To realize a solventless, electron beam-cured magnetic tape manufacturing process a number of materials problems must be solved. First, a mixture of acrylate monomers must be identified that upon electron beam irradiation undergoes free radical polymerization to give a binder polymer with the requisite mechanical properties. The tensile properties of commercial tape are trade secrets and each tape manufacturer has its own specification. For our purposes, we have measured the tensile properties of a unpigmented, commercial, organic solvent-based binder system and found a tensile strength of 18 MPa, a Young's modulus of 710 MPa, and an elongation at break of 60%. These will be used as a guide for identifying electron-beam cured binders. The binders must provide good adhesion between the magnetic coating and the polyester base film to meet the ISO specification of a peel force of 0.96 N for 8 mm wide tape in a 180° peel test.² The particle loading in magnetic tape is about 30 volume percent, which limits the amount of liquid monomer that can be used in the coating fluid. This limits our ability to dilute the coating formulation to the desired viscosity and we anticipate a theology problem with the coating fluid. Another problem is cupping, which is a curling of the tape about an axis parallel to the longitudinal direction. Cupping arises from the stresses developed in the tape due to excessive shrinkage in the coating during curing. Cupping can lead to edge wear, generating debris that spreads throughout the tape system. After the tape has been coated and cured, the next process step in calendaring to compact the coating and impact a smooth surface finish. The binder must be designed so that the electron beam-cured films can be calendared. An additional consideration is the toxicity of the monomers. We do not want to solve an air pollution problem, but create a worker exposure hazard problem. Solving these problems would provide the magnetic tape industry with a convincing case that a solventless magnetic tape coating process is feasible.

ACRYLATE BINDERS

We have identified some promising formulations that contain mixtures containing monoacrylates, diacrylates, triacrylates and acrylate-terminated urethane oligomers.³ The aliphatic urethane diacrylate oligomers were Ebacryl 8402, from UCB Radcure, and CN 965 A80, from Sartomer, added strength to the cured coatings. The acrylate monomers were chosen to minimize viscosity, allow fast curing, with low shrinkage and low toxicity. The diacrylates and triacrylates increased the curing speed. The monoacrylates were reactive diluents that lowered the viscosity. The tensile strength for all formulations, except one, exceeded our target of 19 MPa. Only one

formation had a Young's modulus that exceeded our specification of 710 MPa. The adhesion problem was solved earlier by irradiating the base film, immediately prior to coating.⁴ We chose a formulation containing 31% CN 965 A80, 62% propoxylated neopentyl glycol diacrylate (SR 9003), 3.5% highly ethoxylated trimethylolpropane triacrylate (SR 9035) and 3.5% isobornyl acrylate (SR 506A), to begin particle dispersion experiments. A preliminary accelerated aging study of an electron beam-cured acrylate binder formulation, exposed to 60°C and 90% relative humidity, Fig. 1, revealed no significant degradation in tensile strength. We conclude that this class of binders does not present an undue environmental stability problem at this time. This issue will be revisited when the binder materials package is better defined.

Fig. 1. Plot of tensile strength as a function of time exposed to 60°C and 90% relative humidity.

DISPERSION RHEOLOGY

Our first attempts to prepare pigmented, solventless formulations demonstrated the severity of the rheology problem. In magnetic tape the signal comes from the magnetic particles and in order to maximize the signal, the particle fraction must be as large as possible. A typical magnetic tape has a 30 volume percent of particles, which means the weight fraction of magnetic particles in the coating fluid must be 80%. The iron particles, with a specific surface area of 54 m²/g, adsorbed all the liquid in our first formulation after predispersing for 1.5 hr in a double planetary mixer. The dispersion had the consistency of brick dust, not at all satisfactory for coating.

A commercial methacrylate functionalized silane coupling agent from Dow Corning, Z-6030, was covalently bonded to the surface of the iron particles. The original purpose was to use the magnetic particles to mechanically reinforce the binder by linking the binder to the particles. The commercial iron particles had a ceramic coating containing alumina. We assumed that the surface contains hydroxyl groups that can react with silanol groups from the coupling agent. After treatment the particles had a saturation magnetization of 110 emu/g, a loss of 17%. A TGA curve showed a 12% weight loss upon heating. We attribute the loss in magnetization to the increase in mass due to the surface coating, not a degradation in the particles.

When dispersions were prepared using the particles treated with Z-6030 at 80 weight percent, a thick paste was obtained. The paste had a viscosity of in excess of 10⁸ cps, too high for coating, but it did show shear thinning. The viscosity of a typical solvent-based coating fluid is in the range of 10³ CPS, with significant shear thinning. When the surface-treated magnetic particles were used at 50 weight percent, we obtained a coating fluid with theological properties, Fig. 2, comparable to a conventional, solvent-based coating fluid. The solventless coating fluid also showed a shear thinning behavior, similar to that observed for conventional coating fluids. The theological properties of magnetic coating fluids are dominated by the magnetic attraction forces between the particles, which increase the elasticity (G') of the coating fluid. The surface treatment occupied surface sites on the particles that would otherwise adsorb acrylate monomers. The surface coating also provided a steric barrier against particles approaching each other, which decreased the strength of the magnetic attraction between particle, thus decreasing the elasticity of the fluid. This particle surface treatment provides us with a potential means of solving the dispersion and rheology problem.

Fig. 2. Frequency dependence of the elastic modulus (G') and viscous modulus (G'') for conventional solvent-based and solventless magnetic dispersions.

ECONOMIC ANALYSIS

We have estimated the costs of our solventless, electron beam cured acrylate magnetic tape manufacturing process. The motivation was to determine whether the operating cost of the solventless process would preclude its adoption by the industry. Earlier we had compared the hourly operating costs of a conventional solvent-based process with our waterborne process and determined that the waterborne process had a 15% lower operating cost.¹ Here we use that analysis as a basis for comparing our solventless process with a conventional process. In table 1 is a comparison of the hourly operating costs for the conventional solvent-based and our solventless

process. In all cases the costs are dominated by the materials costs. For the solvent-based process we considered the case of no recycle and the case where the solvents were captured, purified and recycled. Clearly for the solvent-based process, recycling pays, as it lowers the materials cost to \$1570 per hour while only adding \$13.56 per hour. For the solventless process the hourly materials costs are lower, largely because the solvents are eliminated. By our preliminary analysis the solventless acrylate process is the lowest cost. A problem with this analysis is that we assumed that the cost of the particles was the same for all cases. However, our research has indicated the need to surface treat the particles which will increase the cost of the solventless process. If the surface treatment increased the particle price by 10%, then the overall cost of the solventless process would be \$1616 per hour, higher than the cost of the solvent-based process with recycle. However, our analysis for the solvent-based process does not include the cost of curing the tape, which is a thermal process done by sitting in a curing room over night. It is difficult to get information about the cost of this process step. The solvents used in conventional magnetic tape coating operations are regulated under the Clean Air Act Amendments, RCRA and TSCA. In addition to the engineering controls required to safeguard the workers and the environment, these regulations require compliance monitoring and reporting. We assume that an operation that uses our solventless process would be relieved of the reporting requirements which would lower costs. In addition to eliminating the possibility of air pollution, our solventless magnetic tape manufacturing process would also provide better tape at a lower cost.

Table 1. Comparison of hourly operating costs.

	Solvent-Based (no recycle)	Solvent-Based (with recycle)	Solventless
Materials	\$2022	\$1570	\$1481
Dryer Energy	\$7.69	\$7.69	\$0
E-Beam Curing	\$0	\$0	\$0
Nitrogen	\$0	\$0	\$0
Solvent Recovery	\$0	\$13.56	\$0
Thermal Curing	?	?	\$0
Cost of Compliance	?	?	?
Total	\$2030	\$1591	\$1519

ACKNOWLEDGMENTS

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ELIMINATING SOLVENTS AND ACIDS IN WAFER PROCESSING

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INTRODUCTION

Computer chip manufacturing consumes large quantities of liquid solvents and acids for cleaning processing residues from silicon wafers. We describe here a new technology which eliminates these chemicals by enhancing the solubility of these residues and thereby enabling them to be removed with simple DI water rinses. For understanding we begin new technology I will begin with a brief description of the key manufacturing steps which a silicon wafers passes through.

Following this we will describe Dry Plasma Ashing and Etching, the need for usage of these wet chemicals for cleaning operations, and how the shrinking of device dimensions has had a major influence on the dry plasma processes, in particular requiring greater consumption of hazardous and polluting wet chemicals. This will bring us to a discussion of the present-day consumption levels of these chemicals, along with the pollution and waste disposal problems presently encountered.

We then describe the principle of the new process; the present program of introducing the technology to the industry; and the potential reductions in manufacturing costs and pollution burden which can be achieved as the industry changes to this new processing.

We close with a presentation of Scanning Electron Micrographs illustrating the nature of the various residues which must be deal with and how the new process results in a total clean with only DI water rinsing.

FUNDAMENTALS OF DEVICE MANUFACTURING

A silicon wafer is first sliced from an ingot, polished, and cleaned to be ready for chip manufacturing. Dopant impurities are added to selected regions of the chip to modify their electrical properties. Defining these regions is done through lithographic procedures. Photoresist is applied to the wafers, patterned, and the dopants are introduced into the silicon by ion implantation or diffused in a furnace through an oxide mask which has been patterned. In addition thin films of materials are deposited on the wafer and patterned in like manner through etching processes. Each of these tests requires the application, and the subsequent removal of a photoresist mask.

It is essential that all components of the resist mask be totally removed from the wafer before the next process step can proceed. Impurities left behind will damage the electrical performance of the finished chip. Because the resist is designed to withstand harsh ion implantation or etching environments it becomes difficult to remove after the processes are completed. Hence the adoption of strong solvents and acids by the industry to assure total removal of any residuals from the resist.

INTRODUCTION OF DRY ASHING AND ISOTROPIC DRY ETCHING

In late 1968 dry plasma ashing was introduced to the industry. This is a dry plasma process utilizing oxygen gas, under vacuum of a few torr, to ash off the photoresist material utilizing the reactivity of atomic oxygen and ions made in the plasma, at temperatures around 250 to 300C. This process offered the opportunity to remove the bulk of the photoresist mask in a dry process using no wet chemicals and was very quickly adopted by the industry because of the major cost savings. However, this process did not leave a clean resulting wafer. Residues from the process-damaged resist always remained on the wafer and still required exposure to the strong acids or solvents to assure their total removal. Thus the process of dry plasma ashing became always associated with follow-on wet processing steps and to this day remains the conventional procedure for resist removal throughout the entire industry.

In the early 1970's dry plasma etching was introduced to the industry. In this process gases such as CF_4 or SF_6 were used in the plasma where free F atoms would be created. This atomic fluorine reacted with silicon compounds to form the gas SiF_4 which enabled the etching away of thin films of polysilicon, silicon nitride and silicon dioxide thereby further replacing the use of acids which were the common etchants at that time. The etching, both dry plasma and wet chemical, was isotropic in nature. This means that there would always be a pattern undercut of the photoresist equal to the depth of the film being etched. For the device geometries of the 70's this was quite adequate and plasma dry etching along with plasma ashing became well ensconced in the

industry.

SHRINKING DEVICES AND ANISOTROPY IN ETCHING

The dramatic pace of device shrinking which started in the 1980's fired the need for anisotropic plasma etching to be able to define patterns with finer degrees of dimensional control. This need occurs when the lateral dimensions of the features of the devices become comparable to the vertical dimensions of the feature being defined.

The etcher manufacturers successfully developed these processes. However, anisotropic etching included the need to form heavy polymeric residues on the pattern sidewalls to protect the patterns from lateral etching. These polymers are essential to etch anisotropically. As the polymers are grown during the etching process they incorporate etch products within their structure. When the time comes to remove the resist mask, these polymers which contain metals and complex organic structures are not removed by conventional ashing and have been an important reason for increased usage of solvents and acids following the ashing operation. Examples of these deposited polymers are illustrated in figure 1.

EVOLUTION OF CONVENTIONAL ASHING TO 1998

Conventional ashing, as indicated as having been introduced some 30 years ago in 1968, was based primarily on ashing with oxygen. This technology saw very little change until the middle 1980's, when the idea of removing the wafers outside of the plasma (now generated at microwave frequencies as well as RF) and then providing external-sources of heat to activate the chemistry, thereby totally isolating the wafers from any electrical charge damage possibility from the plasma, became established. However, although the hardware configurations were changed, the basic Oxygen chemistry of the process remained the same until the early 90's when research began on the process methodology to be discussed here today.

INTRODUCTION OF enviro™ PROCESSING

Shown in figure 2 is the reported level in recent years of consumption by the US semiconductor industry of the liquid chemicals utilized to manufacture silicon chips. The bulk of the solvent, sulfuric acid, and hydrogen peroxide usage is for the removal of photoresist and its residuals as described above. Thus a major fraction of these chemicals are addressed by the subject we are discussing here.

The average cost for DI water is estimated (Sematech Figures, private communication) at \$0.10 per gallon including equipment capitalization and source material as contrasted to that of typical solvents and acids which can run from \$20 to \$40 per gallon in addition to equipment costs and disposal costs. It is clear that there are substantial costs to be saved.

The materials which we are removing from the wafer surface typically comprise bulk photoresist, primarily organic in nature; plus plasma-formed organic polymers containing inorganic entrapped constituents such as metal chlorides, fluorides, or bromides. Many of these materials in themselves are water soluble, such as the metal chlorides and often fluorides. The organic structures are typically reacted to form CO, CO₂, and water products. Conventional ashing processes which employ oxygen chemistry and operate at 250-300 degrees C, result in oxidation of the metal constituents, thereby converting the original compounds to insoluble and refractory oxides trapped in the organic matrices

The ability to attack these materials with a dry plasma process at essentially ambient temperature would enable removal of the organic matrix leaving the inorganics in water soluble form. This, then, is one important key to the enviro™ process: namely, removal of organics at ambient temperature. There are two methods which we use to do this. One employs a microwave plasma, remote from the wafer to avoid any heating, but rich in atomic fluorine and oxygen. This process very rapidly attacks hydrocarbon organic materials through fluorine abstraction of the hydrogen with subsequent reaction of other constituents with the oxygen. The effect is the dry removal of the organic matrix leaving a residual water-soluble ash of chlorides, fluorides, etc.

This processing is done in a plasma reactor shown in figure 3. The microwave plasma is generated as indicated, and the active radicals flow through the chamber inlet into the aluminum plasma reactor. There is no external heating in this case. The active radicals flow over the wafer and remove the organic matrix materials. Depending upon the sample, however, the structure of the polymers is sometimes such that this process is not adequate to break down the polymer and additional energy is required to initiate reactions.

In this instance we can also employ a very low bias voltage RIE plasma step which through the ion bombardment of the surface can provide adequate energy to initiate ashing reactions yet soft enough to avoid oxidation of any metals or decomposition of any chlorides. Again, then, the result is a totally water soluble residue readily removed with DI rinse.

At the present time we are working with several companies who are evaluating these new processes in their manufacturing lines. Such evaluations are costly and time consuming. "Lots" of wafers must be split at each process step where this new process is used. Half of the lot passes through the conventional process and half the lot passes through the new process. The lots are then combined and processed jointly until the next new process step; the lot is then split again and then recombined as before. At each step along the way standard device inspections and tests are performed to watch out for any problems possibly initiated by the new process.

Each process step where the new process is used is evaluated as a single step and then up through multiple steps where the entire manufacturing scheme has been evaluated. Completed devices must be tested electrically for initial performance; they must also be life tested to be sure that no long-term reliability problems are initiated by the new process. Many months are consumed to do these studies. We anticipate that when these evaluations are successfully completed the information will be released to the industry. Meanwhile we are continuing to work with additional manufacturers who are interested in this new technology and anticipate the time when a major reduction in industry consumption of these solvents and acids will begin to become evident.

Figure 1.

Figure 2.

Figure 3.

ELECTROLYTIC PRODUCTION OF NEODYMIUM WITHOUT EMISSION OF PFCs

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ABSTRACT

Electrolytic deposition from a molten fluoride electrolyte is an efficient method to produce neodymium metal or alloys. EMEC Consultants, with financial support of the U. S. Department of Energy, developed a process using neodymium oxide as the cell feed and avoiding the emission of perfluorinated carbon compounds (PFCs) in the off gases by operating at low anode potentials.

A somewhat "easier" approach, using higher cell voltages, is associated with the anodic formation of PFCs, known to be potent greenhouse gases. Based on patent literature and other information, it has to be assumed that this approach is practiced commercially. It is estimated that effectively as much as 1 % of Japan's output of greenhouse gases may originate from this rare earth metal production, and adoption of a low-voltage process to produce neodymium is recommended.

INTRODUCTION

The predominant use of neodymium is in permanent magnet materials, in NdFeB alloys. This market continues to grow at a rate of approximately 12 % per year. Main uses are in the computer industry, but new applications such as servo motors and automobiles (ABS sensors, logo meters, loud speakers) are increasing.

While other approaches are also practiced, the electrolytic production of neodymium and neodymium alloys is particularly cost-effective. There are the following possibilities:

using the chloride: $2 \text{NdCl}_3 \rightarrow 2\text{Nd} + 3\text{Cl}_2$
 using the fluoride: $4 \text{NdF}_3 + 3 \text{C} \rightarrow 4\text{Nd} + 3\text{CF}_4$
 using the oxide: $2 \text{Nd}_2\text{O}_3 + 3 \text{C} \rightarrow 4\text{Nd} + 3\text{CO}_2$

Of these possibilities, the direct electrolysis of the oxide is particularly attractive, as no intermediate product has to be manufactured to be fed to the electrolysis.

ELECTROLYSIS OF NEODYMIUM OXIDE

The electrolysis of neodymium oxide presents several challenges due to a particular chemistry. Neodymium oxide can be dissolved in fluoride melts, similar to aluminum oxide in the Hall-Héroult process to produce aluminum. The solubility of neodymium oxide, however, is only moderate, about 1 to 2 wt%. Reoxidation of the metal product occurs and is fostered by the presence of oxide; it leads to the formation of nasty oxyfluoride sludges (by a mechanism not encountered in aluminum electrolysis).

The tendency to anode effects exists in melts of low neodymium oxide content (at anode effect the cell current at a given cell voltage drops dramatically and practically no metal is produced). There are conditions, however, where the anode effect results in only partial decay of the current, and the current increases again at moderately higher voltages, as shown in Figure 1¹.

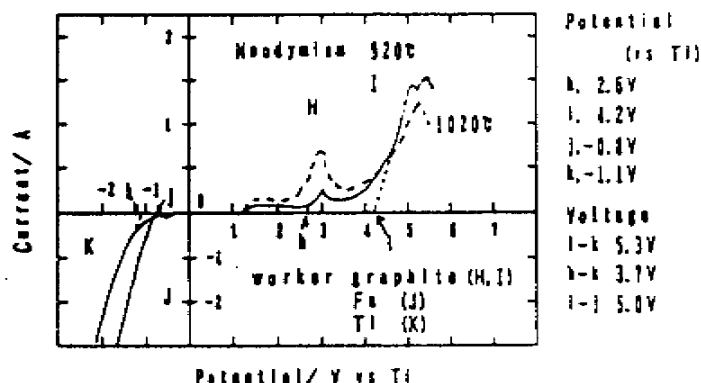


Figure 1. Polarization curves from literature¹

It is in this regime of moderately higher cell voltages that industrial oxide electrolysis has been advocated². EMEC Consultants conducted successful experiments employing such conditions, but the analysis of the off-gases revealed large contents of the perfluorocarbon compounds CF₄ and C₂F₆. This is indicated in Figure 2.

The analysis of the off gases in early Bureau of Mines experiments³ indicated the presence of CF₄, as the ratio of CO, CO₂ and CF₄ is given as 6.5:1:1. This corresponds to about 12 % PFC content, whereby the C₂F₆ content

may not have been determined. Bertaud² obtained 12 % CF₄, 8 % CO₂ and 80 % CO, and the collection and recovery of CF₄ by liquefaction and distillation was suggested. High cell voltages are generally indicated in the patent literature; as an example, Tamamura⁴ reports an average cell voltage of 6 to 8 V, regardless whether he electrolyzed with 2 % Nd₂O₃ in the electrolyte or without Nd₂O₃. In another publication, he mentions that the electrode is consumed, while NdF₃ is electrolyzed and concludes that fluorocarbon compounds are generated.

SIGNIFICANCE OF THE EMISSION OF PFCs

There are indications that both the high-voltage oxide electrolysis and a pure fluoride electrolysis are practiced commercially. It is estimated that up to 2,000 t/yr of neodymium are produced in Japan by these processes. An assessment of potential green- house gas emission shows that the impact on global warming may be substantial. If 1,000 t/yr Nd are produced at a current efficiency of 70 %, with 20 % CF₄ emitted into the air, an emission amounts to 130 t CF₄ annually. A production of an equal amount of neodymium by fluoride electrolysis would add 460 t/yr CF₄. Combining 1,000 t/yr Nd each produced by the two approaches, the Japanese industry, therefore, could emit as much as 600 t CF₄ (to represent all PFCs) annually, if emissions are not being controlled.

Figure 2. Composition of anode gases in an experiment electrolyzing neodymium oxide

This amount is actually of the same magnitude as the consumption of CF₄ by the Japanese semiconductor industry. Considering a factor of 6,500 for the potency of CF₄ as greenhouse gas compared to CO₂, this emission could have a global warming effect equivalent to that of 3.9 million tons of CO₂. It could amount to 1 % of Japan's total effective emission of greenhouse gases.

It appears recommendable that practices in the Japanese neodymium production industry are examined and, if PFCs are emitted, that off-gases be treated or a low-voltage technology be introduced.

AN ALTERNATIVE: LOW-VOLTAGE ELECTROLYSIS

In further experimentation, EMEC Consultants pursued an approach to produce iron-neodymium alloy at low voltage, at which no PFC compounds are formed. With proper electrochemical engineering measures, problems at the cathode and the product pool were minimized. No anode effects occurred. Current efficiencies exceeded 60 percent over a period of 96 hours. This technology is ready to be implemented on the pilot scale.

This development was supported by the U. S. Department of Energy, Cooperative Agreement No. DE-FC07-91ID13104. For non-technical reasons, plans for the scheduled pilot phase were cancelled.

SUMMARY

The electrolytic production of neodymium metal and alloys using fluoride electrolytes is a cost-effective production process. Literature and other information suggest that when this technology is practiced industrially, perfluorocarbon compounds are emitted, a fact whose environmental implications do not seem to have been discussed in the literature. Although, overall, not a high-volume industrial process, it is conceivable that about one percent of Japan's effective greenhouse gas emission presently results from this process. Substitution of a low-voltage technology may be a most cost-effective way to correct the situation. Any new neodymium production capacity — anywhere in the world — should use a technology which avoids the emission of PFCs into the atmosphere.

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SAFER CHEMICALS

CHROME-FREE SINGLE-STEP *IN-SITU* PHOSPHATIZING COATINGS

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ABSTRACT

The current organic coating on metals involves a multi-step process and considerable energy, labor, and control. In particular, the phosphate/chromate pre-treatment step is an error-prone process that requires time-consuming bath controls and also leads to possible surface contamination by parts carrying impurities from bath to bath, and it generates toxic wastes such as chlorinated solvents, cyanide, cadmium, lead, and carcinogenic chromates. The green chemistry technology of *in-situ* phosphatizing coatings (ISPCs) developed in our laboratory is a one-step self-phosphating process. The unique chemical principle of ISPCs is that an optimum amount of *in-situ* phosphatizing reagents (ISPRs) are pre-dispersed in the desired paint systems to form a stable and compatible one-pack coating formulation. The formation of a metal phosphate layer *in-situ* will essentially eliminate the surface pre-treatment step of employing a phosphating line/bath. The ISPRs form chemical bonds with polymer resin that act to seal and minimize the porosity of the *in-situ* phosphated substrate. The use of chemical bondings to seal the pores of metal phosphate *in-situ* should enhance coating adhesion and suppress substrate corrosion without a post-treatment of final rinses containing chromium (Cr^{6+}).

INTRODUCTION

The current practice of applying state-of-the-art organic coatings to metal substrates is a multi-step process. Normally, the metal surface is cleaned, phosphated or chromated, possibly sealed (with hot water or carcinogenic chromates)^{1,2}, dried, and finally painted. The surface pre-treatment process is error and costly, but it is necessary in the metal finishing industry.³ Unfortunately, multi-step coating technologies produce wastes including organic solvents, heavy metals, and other toxic and deleterious materials.⁴

Recently, *in-situ* phosphatizing coatings (ISPCs) have been developed in our laboratory.⁵⁻¹⁰ In an ISPC, an optimum amount of an *in-situ* phosphatizing reagent (ISPR) is pre-dispersed in the paint system to form a stable and compatible coating formulation.⁵ When a single coat of the *in-situ* self-phosphating paint is applied to a metal substrate, the phosphatizing reagent chemically and/or physically reacts *in-situ* with metal surface to produce a metal phosphate layer and simultaneously form covalent phosphorus-oxygen-carbon (P-O-C) linkages with the polymer resin.^{6,7} Sealing the pores of the metal phosphate layer generated at the metal/paint interface by covalent P-O-C linkages enhances the coating's adhesion and suppresses substrate corrosion without the use of toxic form of chromium (Cr^{6+}).

In this paper, we report the successful application of ISPCs in three commercial paints (Sherwin-Williams Company): a high-solids polyester baking enamel (PERMACLAD® 2500 and 2523), a VOC-free thermoset acrylic latex system (KEM AQUA® 1800T), and a water-reducible alkyd baking enamel (KEM AQUA® 1400). The following tests on ISPCs have been performed: coating storage stability, *in-situ* phosphatization of metal surface, paint film quality and crosslinking density, paint disbonding resistance, cathodic delamination, electrochemical impedance spectroscopy, and salt spray. The results will be discussed in light of the environmental, economical, technical advancements of ISPCs over those of the current multi-step coating practice.

RESULTS AND DISCUSSION

The *in-situ* phosphatizing reagents employed for the formulation of ISPCs were selected from the organic substituted phosphoric acids: RH_2PO_4 and R_2HPO_4 , and phosphonic acids: RH_2PO_3 and R_2HPO_2 , where R = H, alkyl, vinyl, aryl, and polymer chain. The experimental details on paint formulation, phosphate fundamentals, polymer chemistry and corrosion resistance testings have been described elsewhere.⁵⁻¹⁰

The success of the technical development of ISPCs relies on the delicate balancing of *in-situ* phosphatizing reagents to form a stable and compatible paint system. The experimental observations indicated that the ISPC formula remains perfectly sprayable after a long-term storage at room temperature, although a noticeable viscosity change (increase or decrease) from its control formula is recorded, owing to the coating's polymer chemistry (e.g., polymer chain extension)¹⁰ being affected by the ISPRs. The *in-situ* phosphatizing reagent catalyzes the polymer chemistry and simultaneously activates the phosphate chemistry. The result is a "simultaneous" formation of a surface metal phosphate layer and a covalent bonding of phosphorous-oxygen-carbon linkage.⁶ The nature of metal phosphate bondings in ISPCs has been identified by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy combined with

energy-dispersive X-ray spectrometry to be an acid-base type interaction, $\text{P-O}^- - \text{Fe}^{2+}$, rather than an induced dipole interaction of P=O/Fe complex type.⁸⁻⁹ A covalent P-O-C linkage is evidenced in FTIR spectrum at 934 cm^{-1} , providing a strong coating adhesion at the polymer/phosphate interface. It is generally believed in surface coating that a good coating/substrate adhesion is necessary for a good protective coating performance. The enhanced coating adhesion of ISPCs has been verified by salt water immersion tests and cathodic delamination measurements.¹⁰

Electrochemical impedance spectroscopy (EIS) has been proven to be a powerful tool for the determination of coating protective performance and undercoated metallic corrosion. Figure 1 shows the Bode-magnitude plots for KEM AQUA® 1800T control latex coating on untreated bare CRS (curve 1a), iron phosphated B-1000 (curve 1b) and iron phosphated and Parcolene 60 chromated BD+P60 (curve 1c) panels. In the low frequency region of

Figure 1, the three Bode-magnitude curves begin to split as the impedance ($|Z|$ in $\text{ohm}\cdot\text{cm}^2$) is more and more affected by the coating-substrate interface response to the AC signal. In general, all curves deviate from the linear relationship of $\log |Z|$ vs. $\log f$ (f = frequency in hertz), and become more frequency-independent. A frequency-independent horizontal line in the Bode-magnitude diagram is a characteristic of pure resistor. At $f = 1.0 \times 10^{-2}$ Hz, the $|Z|$ value is measured as 7.2×10^7 , 2.6×10^8 , and $5.3 \times 10^8\text{ ohm}\cdot\text{cm}^2$ for curve 1a, 1b, and 1c, respectively. The results follow nicely the expectation that the effect of phosphate pre-treatment of CRS will triple the $|Z|$ value, and that of additional chromate rinse on B-1000 substrate will further double the impedance value of latex coating.

Figure 2 shows the Bode-magnitude plots of latex-ISPCs coated on bare CRS (curve 2A), B-1000 (curve 2B) and BD+P60 (curve 2C) coupons. All three curves are apparently overlapping throughout the experimental frequency range, and all behave as a pure capacitor (i.e., the curve of $\log |Z|$ vs. $\log f$ gives a straight line with a slope of -1). At $f = 1.0 \times 10^{-2}$ Hz, the $|Z|$ value is measured as 1.0×10^{10} , 1.2×10^{10} , and $1.4 \times 10^{10}\text{ ohm}\cdot\text{cm}^2$ for curve 2A, 2B, and 2C, respectively. This observation clearly indicates that the paint film of latex-ISPC on metal substrates (both untreated and pre-treated) can be classified as providing excellent corrosion protection. A more than two-order of magnitude increase in paint film resistance $|Z|$ is observed for latex-ISPC (curve 2A) as compared to the control latex formula (curve 1a) on bare CRS, providing evidence of the successful generation of *in-situ* metal phosphate layer at the metal/coating interface. The results strongly support that the technique of *in-situ* phosphatizing coating can be developed into an effective alternative process to the conventional substrate surface pretreatment, a costly, error-prone, and environmentally unfriendly process.

Verification of the performance of a coating meant to endure for long periods of time under various environmental conditions represents a major technical challenge. As an example, Figure 3 shows the results of 100 hours salt spray (fog) test for the control alkyd formula (KEM-AQUA® 1400, top three coupons) and water-reducible ISPC (bottom three coupons) on bare CRS (panels a and b), B-1000 (panels c and d) and BD+P60 (panels e and f). On all three substrates, the control alkyd coating provides much less corrosion protection. At the same time, very little paint deterioration is evidenced in the water-reducible ISPC formula. The water-reducible ISPC applied on bare CRS panel (Figure 3b) has out-performed the control alkyd paint on iron phosphated and chromated substrate (Figure 3e), indicating that it is feasible to substitute the single-step ISPC technique for the traditional multi-step surface pre-treatment/coating process, making it obsolete. Similarly, Figure 3f indicates that the best corrosion protection paint film was produced by a combination of water-reducible ISPC with the BD+P60 substrate that, together, produce an extra passivation effect.

SUMMARY

The green chemistry of ISPCs combines surface pre-treatments, primer and topcoat into a single application, in which phosphate chemistry and polymer chemistry take place independently, but simultaneously. The technology of ISPCs is **a smarter chemistry** because the "simultaneous" chemical reactions of *in-situ* phosphatizing reagents (ISPRs) with metal substrate and polymer resin form a defect-free superior surface coating without contamination of the pre-treatment by parts carrying impurities from bath to bath. The technology of ISPCs is **a cheaper chemistry** because the elimination of the phosphating/chromating line/bath (an operation costing between \$300 K to \$400 K per unit per year) saves time, energy, materials, and labor. The technology of ISPCs is **a cleaner chemistry** because the toxic wastes (such as chlorinated solvents, cyanide, cadmium, lead, and carcinogenic chromates) produced from the phosphating/chromating bath/line are avoided. With its use, landfills and treatment centers would see a reduction in hazardous waste, and transportation of such waste would be avoided.

Figure 3.

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IN VIVO SYNTHESIS OF INSECT SEX PHEROMONE PRECURSORS IN YEAST

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ABSTRACT

Elucidation of the chemical structures that constitute the sex pheromones of hundreds of species of insects has enabled the development of a highly selective, nontoxic, environmentally benign pest control approach based on mating disruption. A major limitation to the commercial success of this approach is the requirement of high chemical and stereo-specific purity, which makes pheromones expensive to synthesize by conventional chemistry. Toward the goal of developing lower cost biosynthetic routes, we are pursuing research to develop strains and process steps employing recombinant yeast expressing moth pheromone biosynthetic desaturases possessing unique catalytic specificities for the formation of key unsaturated intermediates.

INTRODUCTION

Need for less toxic insect pest control strategies. Insect pests affect virtually every major crop throughout the world, and cause substantial losses to human food and fiber supplies. At present, broad-spectrum neurotoxic insecticides are the principal tools for controlling the insect pest species responsible for these losses. Despite their dominant position in the worldwide market for insect pest control products, insecticides have a number of serious drawbacks, which include their toxicity to humans and non-target organisms as well as their persistence in the environment. Another major problem associated with their use is the tendency of many pest species to develop genetically based resistance to the limited number of compounds that can be used against them, in some cases leading to catastrophic control failures. Thus, the development of novel pest control products that are specific, nontoxic and cost-effective is both desirable and necessary to ensure the continued productivity of worldwide agriculture and a safe environment.

Because of the seriousness and scale of environmental and human health problems associated with insecticide manufacture and use, there has been considerable effort expended by government and public research universities to develop and implement integrated pest management (IPM) approaches that attempt to reduce the reliance on toxic chemicals for insect control. Such IPM strategies typically incorporate several pest control techniques, such as the use of pest-resistant host plants and more intensive cultural practices in conjunction with the use of biological agents to kill insect pests. The latter include classical "biological control agents" such as predatory or parasitic insects as well as pathogenic bacteria and viruses that infect and kill their insect hosts. Suppression of insect pest populations below economic thresholds can also be achieved by interfering with insect reproduction using techniques such as sterile male release and mating disruption mediated by insect pheromones. The long-term goal of our research effort is to develop the latter environmentally benign insect control approach into one of the major components of future IPM programs.

Use of pheromones for insect pest control. Many insect species have evolved a mate recognition system based on chemical communication. For example, in the Lepidoptera (moths), which includes many pest species, sexually mature females release a volatile sex pheromone. Male moths recognize the unique chemical signature of the pheromone released by a female of its own species, and fly upwind in an effort to locate the "calling" female and copulate with her. Characterization of the pheromones of hundreds of moth species has revealed a remarkable diversity of unique chemical structures, the vast majority of which are aliphatic compounds having a specific chain length, location of unsaturation and a terminal functional group such as aldehyde, alcohol or acetate. Knowledge of the specific structures of insect pheromones has enabled their chemical synthesis, which has provided the basis for their commercial use to suppress pest populations through mating disruption. The use of pheromones to control insect pests has several major advantages over chemical insecticides. In particular, pheromones are nontoxic, highly selective and environmentally benign. From the standpoint of regulatory considerations, many pheromone products are already registered for use, and the expense and time required to register new ones are minimal compared to insecticides.

Economic factors limit the potential use of pheromone-based insect control strategies. Despite the many

advantages that pheromones possess, they have gained only a minor market niche in the \$6 billion worldwide market for insect control products, largely because of their high cost of synthesis via conventional chemistry. In contrast to pheromone syntheses *in vivo* which are enzymatically synthesized from readily available saturated fatty acid precursors, current approaches for the commercial production of pheromones employ traditional synthetic chemical routes. Because pheromones require very high purity to elicit an insect's response, these syntheses are expensive and difficult. In general, coupling reactions that use moisture- and oxygen-sensitive organometallic reagents are required to establish the correct position of the double bond. These coupling reactions require elaborate manipulations and especially pure feedstocks and solvents, and generate large amounts of organic wastes that require treatment. Thus the coupling reactions typically drive the cost of the process. Moreover, since pheromones are effective in such small quantities (typically a few grams per acre), the cost of pheromone production via standard techniques is unlikely to decrease significantly from volume production.

SUMMARY

Development of low-cost, biologically-based routes for pheromone synthesis. Our research addresses the problem of the high cost of pheromone synthesis by developing the components of an alternative biologically-based production process. I will describe our experiments involving the cloning of genes encoding moth pheromone desaturases possessing unique catalytic mechanisms, the biochemistry of these enzymes, which is similar to the ubiquitous acyl-CoA desaturases of animals and fungi to which they are related, and the strategy we are pursuing to achieve the formation of high value unsaturated pheromone intermediates in recombinant yeast strains expressing these genes.

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DESIGN, SYNTHESIS AND PROPERTIES OF FIRE-SAFE POLYMERS AT THE UNIVERSITY OF MASSACHUSETTS, AMHERST

Phillip R. Westmoreland, Richard J. Farris, William J. MacKnight, Simon W. Kantor,
Thomas J. McCarthy, Bruce M. Novak and Alan J. Lesser

Fire in an enclosed and inescapable area is a major threat to human life. The interior of an aircraft cabin represents such an environment, as do submarines, ships and high rise buildings. The utilization of lightweight polymeric fabrics and composites adds to this threat because of their potential for rapid combustion and the release of toxic by-products. Such is the case for aircraft where there exists a large fuel load of combustible plastics utilized in the interior cabins. The University of Massachusetts, in conjunction with the Federal Aviation Administration and Industry, have joined together in a multi-year, multi-investigator program in an attempt to create the next generation of Fire-Safe materials. An overview of this program and the initial results will be presented. The program encompasses computer modeling and simulations for predictive design, synthesis of novel fire-resistant polymers, alternate methods for flame resistance and retardency, new analytical techniques and equipment for studying and evaluating combustion, characterization and performance properties of the new materials. The program is aimed at understanding the basic principles of polymer combustion to allow for safer design of Fire-Safe polymers.

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**PROCESS
ANALYTICAL
CHEMISTRY**

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ON-LINE ANALYZERS FOR IMPROVED PROCESS DEVELOPMENT

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Automated process analyzers are often adapted for monitoring manufacturing wastes. By further application of analyzers within a process control strategy, waste and energy costs can be controlled rather than just monitored, and quality and yield can be improved. New process development represents a "third generation" use for process analyzers. They facilitate real-time adjustment of pilot process operating conditions, resulting in faster scale-up to more efficient and cleaner manufacturing. In addition, analyzer instrumentation and sample systems can be tested and modified for better integration with the full-scale process. Our program currently utilizes online Mass Spectrometry (MS) and Fourier-Transform Infrared (FTIR) Spectrometry for rapid measurements over wide dynamic ranges for analysis of both major and minor process stream constituents. In addition, these technologies offer rapid identification of unknown components by automated comparison of spectra with computer reference libraries.

ANALYSIS OF ADDITIVES IN POLYETHYLENE BY MICROWAVE ASSISTED SOLVENT EXTRACTION AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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Speed and accuracy of additive analysis in polyethylene are critical to ensuring that finished products have the specified performance characteristics. The analytical process requires solvent extraction of the polymer followed by HPLC analysis. The traditional reflux apparatus used for sample preparation is time consuming, uses large volumes of solvent, and is costly. Microwave Assisted Solvent Extraction utilizes small solvent volumes and control of extraction solvent temperatures above their normal atmospheric boiling points, dramatically shortening the time and cost required to extract additives from polyethylene.

A microwave system and vessels capable of safely operating at elevated temperatures and pressures, have been developed. Microwave energy is utilized to quickly and efficiently elevate solvent temperatures above their normal atmospheric boiling points. Design and safety features of the microwave system, and solvent temperature and pressure parameters are presented.

Applications are demonstrated in preparation of samples for analysis by HPLC. These applications include extraction of additive packages from Low Density Polyethylene, High Density Polyethylene, Low Linear Density Polyethylene and Polyethylene/Ethyl Vinyl Acetate. Analyte recoveries compared to standard reflux extraction are shown.

**PROCESS ANALYTICAL CHEMISTRY IN WASTE MINIMIZATION
AND SPILL PREVENTION AT EASTMAN CHEMICAL COMPANY**

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Eastman Chemical Company has implemented process analytical chemistry in identifying and preventing accidental discharges, and in driving its waste minimization initiative. This work describes the sewer monitoring program that has been developing over several years. Both on-line and laboratory analyses are utilized in monitoring the non-contact cooling water sewer and the process wastewater sewer. Practical issues of sampling and analyzing dirty aqueous streams have been addressed. This program has improved the quality of information provided about types and amounts of waste in the influent to the waste treatment facility. The monitoring also provides rapid detection of accidental discharges and a means to respond quickly to prevent an upset of wastewater treatment and to prevent any impact on the river.

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Stephanopoulos, G.	1997	169	Williams, D.E.	1997	45
Stradi-Granados, B.A.	1997	21	Woomer, C.G.	1997	53
Strazisar, S.A.	1997	53	Wright, L.J.	1998	206
Subramaniam, B.	1998	241	Wyman, C.	1998	191
Subramanian, R.	1998	205			
Suckling, I.	1998	206	Yachandra, V.K.	1998	243
Sullivan, C.S.	1998	207	Yu, T.	1998	259
Suroka, J.	1997	106			
Svirkin, Y.Y.	1997	36	Zhao, R.	1998	215
Swift, G.	1997	36	Zhu, T.	1997	77